Notes on Brownian motion and related phenomena

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In this article we explore the phenomena of nonequilibrium stochastic process starting from the phenomenological Brownian motion. The essential points are described in terms of Einstein's theory of Brownian motion and then the theory extended to Langevin and Fokker-Planck formalism. Then the theory is applied to barrier crossing dynamics, popularly known as Kramers' theory of activated rate processes. The various regimes are discussed extensively and Smoluchowski equation is derived as a special case. Then we discuss some of the aspects of Master equation and two of its applications.

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I. BROWNIAN MOTION : EINSTEIN'S THEORY

A. Introduction

The so-called Brownian motion was described for the first time in the year 1828 by the botanist Robert Brown. In investigating the pollen of different plants he observed that this become dispersed in water in a great number of small particles - the pollen grains. These were perceived to be in uninterrupted and irregular swarming motion. As the phenomenon repeated itself with all kinds of organic substances, he thought that he had found in these particles the 'primitive molecule' of living matter. He also found that all kinds of inorganic substances presented the same phenomenon and drew the conclusion that all matter was built up of 'primitive molecules'.

Of the authors who carried out investigations on the Brownian movement before Einstein, we mention : Regnault (1858), Weiner (1863), Jevons (1870), Dancer (1870) and Delsaux (1877).

The first precise investigation was due to Gouy (1888), who observed that the motion is more lively the smaller the viscosity of the liquid. He also ascribed the motion to the effect of thermal molecular motion of the liquid. Besides Gouy's work there was only other investigation of precise nature by Exner (1900) who showed that the velocity of the movement decreases with the size of the particle and increases with rise of temperature.

Einstein was the first (1905) to formulate a correct picture of the entire problem. We discuss his theory in Sec. 1.2, 1.3, 1.4. and 1.6. [1]

B. The irregular movement of particles suspended in a liquid and its relation to diffusion

(a) Suppose there be suspended particles irregularly dispersed in a liquid. The particles are of microscopically visible size and their movements are of such magnitude that they can be observed under a microscope. We first consider here the irregular movements of particles which arise from thermal molecular movement. This gives rise to diffusion.

Evidently it must be assumed (i) that each particle executes a movement which is independent of movement of all other particles. (ii) The movement of one and same particle after different intervals of time must be considered as mutually independent processes, if we think these intervals are not too small.

We introduce a time interval τ, which is very small compared to observed interval of time, but at the same time large such that the motion executed by a particle in two consecutive intervals τ are mutually independent.

Suppose that there are n suspended particles. In an interval τ, x-coordinate of the single particle will increase by Δ. Δ has a different (positive or negative) value for each particle. For the value of Δ a certain probability law will hold. Let dn be the number of particles which experience a displacement between Δ and $\Delta + d\Delta$ in time interval τ. Then,

$$\frac{dn}{n} = \phi(\Delta)\, d\Delta \tag{1}$$

where the total probability is one, i.e.,

$$\int_{-\infty}^{+\infty} \phi(\Delta)\, d\Delta = 1 \ . \tag{2}$$

Here $\phi(\Delta)$ is the probability of jump of magnitude Δ for the particle, ϕ only differs from zero for very small values of Δ and fulfills the condition,

$$\phi(\Delta) = \phi(-\Delta) \ . \tag{3}$$

We confine ourselves to motion in one dimension (x). Let $\nu = f(x,t)$, the number of particles per unit volume. We now calculate the distribution of particles at time $t+\tau$ from a distribution at time t.

We consider two planes perpendicular to x axis at x and $x+\Delta$. Then the distribution at time t and space $x+\Delta$ evolves to a distribution at time $t+\tau$ and at x as follows,

[1] We draw heavily from the two classic papers I and IV of Ref. [1]

$$f(x, t+\tau) = \int_{-\infty}^{+\infty} f(x+\Delta, t)\ \phi(\Delta)\ d\Delta \tag{4}$$

The integration over Δ takes into account of all possible jumps from $x+\Delta$ to x each with a probability $\phi(\Delta)$. Since τ is small we write

$$f(x, t+\tau) = f(x, t) + \tau\ \frac{\partial f}{\partial t} \tag{5}$$

Again since Δ is small

$$f(x+\Delta, t) = f(x, t) + \Delta\ \frac{\partial f(x,t)}{\partial x} + \frac{\Delta^2}{2!}\ \frac{\partial^2 f(x,t)}{\partial x^2} + \ldots \tag{6}$$

Putting (5) and (6) in (4) we obtain

$$\begin{aligned} f + \frac{\partial f}{\partial t}\ \tau &= \int_{-\infty}^{+\infty} f(x,t)\phi(\Delta)\ d\Delta + \int_{-\infty}^{+\infty} \left(\frac{\partial f}{\partial x}\right) \Delta\ \phi(\Delta)\ d\Delta + \int_{-\infty}^{+\infty} \left(\frac{\partial^2 f}{\partial x^2}\right) \frac{\Delta^2}{2!}\ \phi(\Delta)\ d\Delta \\ &= f(x,t) \int_{-\infty}^{+\infty} \phi(\Delta)\ d\Delta + \left(\frac{\partial f}{\partial x}\right) \int_{-\infty}^{+\infty} \Delta\ \phi(\Delta)\ d\Delta + \left(\frac{\partial^2 f}{\partial x^2}\right) \int_{-\infty}^{+\infty} \frac{\Delta^2}{2!}\ \phi(\Delta)\ d\Delta \end{aligned} \tag{7}$$

Since

$$\int_{-\infty}^{+\infty} \phi(\Delta)\ d\Delta = 1$$

and [2]

$$\phi(\Delta) = (-\Delta)\ \ ,\quad \phi(\Delta) \text{ an even function }\ ,$$

i.e., $\int_{-\infty}^{+\infty} \Delta\ \phi(\Delta) = 0$. We obtain

$$\begin{aligned} \frac{\partial f}{\partial t}\ \tau &= \frac{\partial^2 f}{\partial x^2} \int_{-\infty}^{+\infty} \frac{\Delta^2}{2!}\ \phi(\Delta)\ d\Delta \\ \frac{\partial f}{\partial t} &= \left[\ \frac{1}{\tau} \int_{-\infty}^{+\infty} \frac{\Delta^2}{2!}\ \phi(\Delta)\ d\Delta\ \right] \frac{\partial^2 f}{\partial x^2} \end{aligned} \tag{8}$$

Putting

$$D = \frac{1}{\tau}\ \int_{-\infty}^{+\infty} \frac{\Delta^2}{2!}\ \phi(\Delta)\ d\Delta\ \ .$$

We obtain the diffusion equation :

$$\frac{\partial f(x,t)}{\partial t} = D\ \frac{\partial^2 f(x,t)}{\partial x^2} \tag{9}$$

where D is the diffusion coefficient.

Note that both the equations (4) and (9) express the same law of evolution of distribution of particles in space and time. While (4) is of integral form, (9) is a differential equation.

(b) Next problem that we investigate is how the distribution spreads in time. Mathematically speaking, this is an initial value problem.

Let us suppose that at $t = 0$ all the particles are concentrated at a point $x = 0$. This means that the density or the distribution function $f(x,t)$ is infinite at this point and zero everywhere (except this point). We consider the problem of diffusion outward from this point.

[2]The jump of magnitude Δ has no preferential direction

$$\text{At} \quad t = 0 \ , \quad f(x,0) = n\ \delta(x) \tag{10}$$

where by definition

$$\begin{aligned} \delta(x) &= 0 \ , \quad x \neq 0 \\ \delta(x) &= \infty \ , \quad x = 0 \end{aligned}$$

Also we have,

$$f(x_0) = \int_{-\infty}^{+\infty} f(x)\ \delta(x - x_0)\ dx \ .$$

Fourier representation of $\delta(x)$ gives

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx}\ dk \ .$$

Writing $f(x,t)$ as a Fourier transform,

$$f(x,t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx}\ \tilde{f}(k,t)\ dk \tag{11}$$

and putting it in Eq.(9) we have

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx}\ \frac{\partial \tilde{f}(k,t)}{\partial t}\ dk = \frac{D}{2\pi} \int_{-\infty}^{+\infty} (-k^2)\ e^{ikx}\ \tilde{f}(k,t)\ dk \ .$$

Therefore,

$$\frac{\partial \tilde{f}(k,t)}{\partial t} = -k^2\ D\ \tilde{f}(k,t) \tag{12}$$

which can be solved to give

$$\tilde{f}(k,t) = \tilde{f}(k,0)\ e^{-k^2\ D\ t} \ . \tag{13}$$

Since $f(x,0) = n\ \delta(x)$ and using the definition of $\delta(x)$ we have

$$\begin{aligned} n\ \delta(x) &= \frac{n}{2\pi} \int_{-\infty}^{+\infty} e^{ikx}\ dk \\ &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx}\ n\ dk \ . \end{aligned} \tag{14}$$

Again from (11)

$$f(x,0) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx}\ \tilde{f}(k,0)\ dk \ ,$$

hence by (10) we have

$$n\ \delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx}\ \tilde{f}(k,0)\ dk \ . \tag{15}$$

Comparison with (14) gives

$$\tilde{f}(k,0) = n \ .$$

Therefore,

$$\tilde{f}(k,t) = n\, e^{-k^2\, D\, t} \quad . \tag{16}$$

Putting (16) in (11) we get the distribution at t [see Appendix-A for details]

$$f(x,t) = \frac{n}{\sqrt{4\pi\, D\, t}}\; e^{-x^2/4\, D\, t} \tag{17}$$

The above equation shows how the distribution spreads in time (as shown in the figures),

(c) We now calculate the displacement λ_x in the direction of x-axis which a single particle experiences on an average - more accurately expressed - the square root of the arithmetic mean of the squares of the displacement,

$$\begin{aligned}
\langle x^2 \rangle &= \frac{1}{n} \int_{-\infty}^{+\infty} x^2\; f(x,t)\; dx \\
&= \int_{-\infty}^{+\infty} x^2\; \frac{1}{\sqrt{4\pi\, D\, t}}\; e^{-x^2/4\, D\, t} dx \\
&= \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{+\infty} x^2\; e^{-\alpha x^2}\; dx \quad , \quad \alpha = 1/4Dt \\
&= \sqrt{\frac{\alpha}{\pi}}\; (-1) \int_{-\infty}^{+\infty} \frac{\partial}{\partial \alpha} e^{-\alpha x^2}\; dx \\
&= -\sqrt{\frac{\alpha}{\pi}}\; \frac{\partial}{\partial \alpha} \int_{-\infty}^{+\infty} e^{-\alpha x^2}\; dx \\
&= -\sqrt{\frac{\alpha}{\pi}} \frac{\partial}{\partial \alpha} \sqrt{\frac{\pi}{\alpha}} \\
&= \frac{1}{2\,\alpha} \quad .
\end{aligned} \tag{18}$$

Thus $\langle x^2 \rangle = 2Dt$ or

$$\lambda_x = \sqrt{\langle x^2 \rangle} = \sqrt{2\, D\, t} \quad . \tag{19}$$

The mean displacement is therefore proportional to the square root of time. This is a typical characteristic of Brownian motion.

C. Diffusion and mobility

We consider the suspended particles irregularly dispersed in a liquid. We consider this state of dynamic equilibrium, on the assumption that a force k acts on the particles and it depends only on position but not on time. For simplicity, we assume that the force is exerted everywhere in the direction of x-axis.

We can look upon the dynamic equilibrium condition as a superposition of two processes acting in the opposite directions.

(i) A movement of the suspended particle under the influence of the external force k. To be specific we consider a particle moving under the force of gravity k in a liquid. The particle is of spherical form with a radius ρ and the liquid has a coefficient of viscosity κ. When the particle immersed in the liquid is falling under gravitational force k it experiences an opposing force of hydrodynamic origin. When the external force k balances the opposing force, the particle falls with a constant terminal velocity v_0. Thus if the external force of gravity is k and the opposing force is $6\pi\kappa\rho v_0$, then

$$v_0 = \frac{k}{6\pi\kappa\rho} \quad . \tag{20}$$

If ν is the no. of particles per unit volume, then $\nu\, v_0$ number of particles pass a unit area per unit time (or $\nu k/6\pi\kappa\rho$) under the action of external force k.

(ii) The process of diffusion which is looked upon as a result of irregular movement of the particles produced by the thermal molecular movement of the liquid.

If D is the coefficient of diffusion of suspended and μ the mass of a particle, then due to diffusion, the number of particles passing per unit area per unit time is

$$-D\frac{\partial\nu}{\partial x}$$

($-D\frac{\partial\mu\nu}{\partial x}$ grams of particles crossing per unit area per unit time)

Under the condition of dynamic equilibrium we must have

$$\frac{\nu k}{6\pi\kappa\rho} = -D\ \frac{\partial\nu}{\partial x}\ \ . \tag{21a}$$

At equilibrium, since the density under the force of gravity k varies as (Boltzmann distribution)

$$\nu = \nu_0\ \exp\left[-\frac{k(x-x_0)N}{RT}\right] \tag{21b}$$

where N is the Avogadro number and R is the universal gas constant. Putting (21b) in (21a) we obtain,

$$D = \frac{RT}{N}\ \frac{1}{6\pi\kappa\rho} \tag{22}$$

The coefficient of diffusion of the suspended particles therefore depends only on the coefficient of viscosity of the liquid and on the size of the suspended particles.

If $\frac{1}{6\pi\kappa\rho}$ is denoted B ("mobility" of the particle) then (22) may be rewritten as,

$$D = \frac{RT}{N}\ B \tag{23}$$

This is the relation between mobility of the suspended particle and the diffusion coefficient.

D. Determination of Avogadro number

We have found the diffusion coefficient D of a material suspended in a liquid in the form of small spheres of radius ρ as,

$$D = \frac{RT}{N}\left(\frac{1}{6\pi\kappa\rho}\right) \tag{24}$$

Again the mean value of the displacement of the particle in x-direction in time t,

$$\lambda_x = \sqrt{2Dt} \tag{25}$$

By eliminating D we obtain

$$\lambda_x = \sqrt{t}\sqrt{\frac{RT}{N}\frac{1}{3\pi\kappa\rho}} \tag{26}$$

This equation shows how λ_x depends on T, κ and ρ. We will now calculate how great λ_x is for one second. Take

$$N = 6\times 10^{23}$$
$$\kappa = 1.35\times 10^{-2} \text{ poise (water at } 17^\circ c) \quad ; \quad 1 \text{ poise} = 1\text{gm.cm}^{-1}.\text{sec}^{-1}$$
$$\rho = 0.001 \text{ mm}$$
$$\text{R} = 8.31\times 10^{7} \text{ erg.mole}^{-1}.\text{deg.K}^{-1}$$

We get

$$\lambda_x = 8\times 10^{-5}\text{ cm}\ \ .$$

On the other hand the relation (26) can be used for determination of N. We obtain thus

$$N = \frac{1}{\lambda_x^2}\frac{RT}{3\pi\kappa\rho} \tag{27}$$

where λ_x has to be determined experimentally.

E. Experimental confirmation

The first of the investigations confirming Einstein's formula in its original meaning was carried out by Seddig (1908) who look two photograph of an aqueous suspension of cinnabar on the same plate at an interval of 0.14 sec and measured the distance of the corresponding images on the plate. He found that on an average the displacement at different temperatures were inversely proportional to the viscosities as the theory demanded.

Henri (1908) found similarly with the aid of cinematograph records of mean displacement of particles Caoutchone that the time law, x^2 proportional to t, was followed.

The establishment of first complete and absolute proof of the formula lies to the credit of Perrin and his group (1914), who followed the movements of single particle of gamboge or mastic under a microscope and recorded their positions at equal time intervals by means of an indicating apparatus. They determined N and found the value between 56 and 88×10^{22}.

F. Theoretical observations on Brownian motion and the existence of a random force

It is now well established that irregular movements of the suspended particles in a liquid are caused by thermal motion of the molecules of the liquid. We now put forward two observations on the Brownian motion from a theoretical point of view to establish the existence of a random force.

(i) From the molecular theory of heat we can calculate the mean value of the instantaneous velocity which the particle may have at the absolute temperature T. Thus the kinetic energy of the motion of a particle is independent of the size and nature of the particle and independent of the nature of its environment, e.g., of the liquid in which the particle is suspended. The mean velocity $\sqrt{\langle v^2 \rangle}$ of the particle of mass m is therefore determined by the equation

$$m\frac{\langle v^2 \rangle}{2} = \frac{3}{2}\frac{RT}{N} \tag{28}$$

with $R = 8.3 \times 10^7$ erg.mole^{-1}.deg.K^{-1} and $N = 6 \times 10^{23}$.

We calculate $\sqrt{\langle v^2 \rangle}$ for particles in colloidal platinum solutions. for these particles we have the mass $m = 2.5 \times 10^{-15}$ gm so that for $T = 292$ K

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3RT}{mN}} = 8.6 \text{ cm/sec} \tag{29}$$

(ii) We will now examine whether there is any prospect of actually observing this enormous velocity of a suspended particle.

If we know nothing of the kinetic theory, we should expect the following thing to happen.

Suppose that we impart to a particle suspended in a liquid certain velocity v by a force applied to it from outside. Then this velocity will die away rapidly on account of the friction of the liquid. The opposing force experienced by the particle is $6\pi\kappa\rho v$, where κ =viscosity of the liquid, ρ =radius of the particle and v is the velocity of the particle. We obtain

$$m\frac{dv}{dt} = -6\pi\kappa\rho v \ , \tag{30}$$

On integration (30) gives

$$v = v_0 \exp\left(-\frac{6\pi\kappa\rho}{m}t\right) \ . \tag{31}$$

From this we calculate the time in which the velocity die away to one tenth of its original value, i.e., $t_{1/10}$. From (31)

$$\begin{aligned} \ln\frac{v}{v_0} &= -\frac{6\pi\kappa\rho}{m}t_{1/10} \\ t_{1/10} &= \frac{\ln 10}{6\pi\kappa\rho/m} \ , \ \text{with} \ \frac{v}{v_0} = \frac{1}{10} \end{aligned} \tag{32}$$

For platinum particles (in water) we have put

$$\rho = 2.5 \times 10^{-6} \text{ cm}$$
$$\kappa = 0.01 \text{ poise}$$
$$m = 2.5 \times 10^{-15} \text{ gm}$$

so that we get

$$t_{1/10} = 3.3 \times 10^{-7} \text{ sec}$$

This means that the particle nearly completely looses its original velocity in the very short time $t_{1/10}$ through friction. But at the same time we must assume that the particle get new impulses from the liquid molecules during this time by some process that is the inverse of viscosity so that it retains a velocity $\sqrt{\langle v^2 \rangle}$ on an average. But since we must assume that the direction and magnitude of these impulses are independent of the original velocity and direction of motion of the particles, we must conclude that the velocity and direction of the motion of the particle will be greatly altered in a very short time $t_{1/10}$ and in a totally irregular manner.

It is therefore impossible at least for ultramicroscopic particle to ascertain $\sqrt{\langle v^2 \rangle}$ by observation.

(iii) Although $\sqrt{\langle v^2 \rangle}$ can not be observed, the change in position in time τ (which is much larger than $t_{1/10}$) can be determined. We have already

$$\lambda_x = \sqrt{\tau} \sqrt{\frac{RT}{N} \left(\frac{1}{3\pi\kappa\rho} \right)} \tag{33}$$

λ_x is the change in x-coordinate in time τ. Then the mean velocity in time interval τ, we define as

$$\frac{\lambda_x}{\tau} = \frac{1}{\sqrt{\tau}} \sqrt{\frac{RT}{N} \left(\frac{1}{3\pi\kappa\rho} \right)} \tag{34}$$

Since an observer can never perceive the actual path traversed in a arbitrary small time a certain mean velocity like λ_x/τ will appear to him as the instantaneous velocity. This is a measurable quantity.

We have already seen that $\sqrt{\langle v^2 \rangle}$ is enormous for a particle when it is suspended in a liquid. On the other hand hydrodynamics tells us that this velocity if imparted to the particle by an impulsive force, will die away very rapidly. Therefore, to maintain the average $\sqrt{\langle v^2 \rangle}$ the particle must experience impulses from the liquid molecules whose direction and magnitude are random. So to reconcile the kinetic theory with hydrodynamics we conclude that there must exist a random force $F(t)$ acting on each particle, so that we write

$$m\frac{dv}{dt} = -6\pi\kappa\rho v + F(t) \tag{35}$$

Eq.(35) is an instantaneous description of motion of the particle. Here the average value of the random force is zero

$$\langle F(t) \rangle = 0 \quad \textit{and} \quad \langle F(t)^2 \rangle \neq 0$$

Eq.(35) is the Langevin equation of motion for the particle. We discuss this equation in the next section.

II. LANGEVIN DESCRIPTION OF BROWNIAN MOTION

A. Introduction

In the studies on Brownian motion we are principally concerned with the perpetual irregular motions exhibited by small grains or particles of colloidal size suspended in a liquid. As is now wellknown, we witness in Brownian movement the phenomenon of molecular agitation on a reduced scale by particles very large on a molecular scale - so large, in fact, as to be readily visible in an ultra-microscope. The perpetual motion of the Brownian particles is maintained by the fluctuations in the collisions with the molecules of the surrounding liquid. Under normal conditions in a liquid a particle will suffer as many as 10^{21} collisions per second and this is so frequent that we cannot talk about separate collisions. And it is impossible to follow the path in any detail

In the absence of any external force, one writes the Langevin equation for a free particle as

$$m\frac{dv}{dt} = -6\pi\eta rv + F(t) \tag{1}$$

η is the viscosity of the liquid, r is the radius of the particle and v the velocity of the particle. According to this equation the influence of the liquid medium on the motion of the particle can be split up into two parts :
• A systematic part $-6\pi\eta rv$, represents a dynamical friction experienced by the Brownian particle.
• A fluctuating force, $F(t)$, which is characteristic of the Brownian motion.
Two assumptions are made

(i) $F(t)$ is independent of v and $\langle F(t)\rangle = 0$.

(ii) $F(t)$ varies extremely rapidly compared to variations of v.

The second assumption implies that the time intervals of duration Δt exist such that during Δt the variations in v to be very small, while during the same interval $F(t)$ may undergo many fluctuations. Although $\langle F(t)\rangle$ is zero, the average $\langle F(t)^2\rangle$ does not vanish since negative swings of $F(t)$ yield positive squared values. Suppose that the minimum time in which $F(t)$ changes appreciably is called the correlation time, τ_c. The average of the product $F(t)F(t')$, vanishes for $|t-t'| > \tau_c$. Hence, $\langle F(t)F(t')\rangle$, the correlation function of the random force is peaked about $t = t'$ and falls off to zero in a time difference $|t-t'| = \tau_c$. If τ_c is less than all other times of interest, e.g., 1/(damping constant), we write

$$\langle F(t)F(t')\rangle = 2\mathcal{D}\delta(t-t') \tag{2}$$

where $\mathcal{D}$ is some constant expressing the magnitude of the fluctuating forces. Eq.(2) along with $\langle F(t)\rangle = 0$, completely defines the Langevin equation (1).

B. General expression for mean square displacement

The Langevin equation for the particle

$$m\frac{dv}{dt} = -6\pi\eta rv + F(t)$$

gives $\frac{d\langle v\rangle}{dt} = -6\pi\eta r\langle v\rangle$ since $\langle F(t)\rangle = 0$.
Therefore,

$$\langle v(t)\rangle = \langle v(0)\rangle \exp\left(-\frac{6\pi\eta r}{m}t\right) \tag{3}$$

Denoting $6\pi\eta r/m = \Gamma$ (damping constant) we rewrite Eq.(1) as

$$m\ddot{x} = -m\Gamma\dot{x} + F(t) \quad . \tag{4}$$

since $\dot{x} = v$, therefore,

$$\ddot{x} = -\Gamma\dot{x} + \frac{F(t)}{m} \tag{5}$$

Multiplying both sides by x we get,

$$x\ddot{x} = -\Gamma x\dot{x} + x\frac{F(t)}{m} \tag{6}$$

$$\begin{aligned} \text{Since} \quad \dot{x^2} &= 2x\dot{x} \\ \text{and} \quad \ddot{x^2} &= 2(\dot{x})^2 + 2x\ddot{x} \\ \text{Thus} \quad x\ddot{x} &= \frac{1}{2}\ddot{x^2} - (\dot{x})^2 \ . \end{aligned}$$

With these relations we rewrite Eq.(6) as,

$$\frac{1}{2}\ddot{x^2} - (\dot{x})^2 = -\frac{\Gamma}{2}\dot{x^2} + \frac{1}{m}xF(t) \tag{7}$$

or

$$\ddot{x^2} - 2(\dot{x})^2 = -\Gamma\dot{x^2} + \frac{2}{m}xF(t) \tag{8}$$

Taking the average we obtain,

$$\frac{d^2}{dt^2}\langle x^2\rangle - 2\langle(\dot{x})^2\rangle = -\Gamma\frac{d}{dt}\langle x^2\rangle + \frac{2}{m}\langle xF(t)\rangle \tag{9}$$

Since[3]

$$\dot{x} = v \quad , \quad 2\langle(\dot{x})^2\rangle = 2\langle v^2\rangle = 2\frac{k_BT}{m}$$

Also[4]

$$\langle xF(t)\rangle = 0 \quad .$$

Thus from (9) we have

$$\frac{d^2}{dt^2}\langle x^2\rangle + \Gamma\frac{d}{dt}\langle x^2\rangle - 2\frac{k_BT}{m} = 0 \quad . \tag{10}$$

We now solve Eq.(10) to obtain mean square displacement $\langle x^2\rangle$. Put $\frac{d}{dt}\langle x^2\rangle = y$ and $c = 2\frac{k_BT}{m}$, then Eq.(10) gives,

$$\dot{y} + \Gamma y - c = 0 \tag{11}$$

Let $\Gamma y - c = y'$, then

$$\begin{aligned} \dot{y'} + \Gamma y &= 0 \\ \text{therefore} \quad y' &= A\exp(-\Gamma t) \quad , \quad A = \text{constant} \quad . \end{aligned} \tag{12}$$

At $t = 0$, $y' = A$, hence

$$\begin{aligned} &\Gamma y - c = A \\ &\text{or} \quad A = -c \;\; ; \;\; c = 2(k_BT/m) \end{aligned}$$

From (12)

$$\begin{aligned} \Gamma y - c &= A\exp(-\Gamma t) \\ y &= \frac{c}{\Gamma} + \frac{A}{\Gamma}\exp(-\Gamma t) \end{aligned}$$

Since, $\frac{d}{dt}\langle x^2\rangle = y$,

$$\frac{d}{dt}\langle x^2\rangle = \frac{c}{\Gamma} + \frac{A}{\Gamma}\exp(-\Gamma t)$$

On integration over 0 to t we obtain,

$$\langle x^2\rangle = \frac{c}{\Gamma}t + \frac{A}{\Gamma^2}(1 - e^{-\Gamma t})$$

Since $A = -c$ and $c = 2\frac{k_BT}{m}$, we obtain

$$\langle x^2\rangle = \frac{2k_BT}{m\Gamma}t + \frac{2k_BT}{m\Gamma^2}(1 - e^{-\Gamma t}) \tag{13}$$

This is the general expression for mean square displacement of a Brownian particle suspended in a fluid.

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[3] By equipartition of energy : $\frac{1}{2}m\langle v^2\rangle = \frac{1}{2}k_BT$, in one dimension

[4] The random force is independent of the position of the particle

1. long time limit

When $t \rightarrow \infty$, $e^{-\Gamma t} = 0$, we obtain the asymptotic behavior,

$$\langle x^2 \rangle = \frac{2k_BT}{m\Gamma} t \;\; \text{(constant part is neglected)}$$

Putting $\Gamma = \frac{6\pi\eta r}{m}$, we have,

$$\langle x^2 \rangle = \frac{2k_BT}{6\pi\eta r} t \quad . \tag{14}$$

The mean square displacement is proportional to time, t by (14). Comparison with Einstein's expression $\langle x^2 \rangle = 2Dt$ gives

$$D = \frac{k_BT}{6\pi\eta r} \quad ,$$

which is the standard expression for diffusion coefficient calculated earlier by Einstein's method.

2. short time limit

When $t \rightarrow$ small, from (13)

$$\langle x^2 \rangle = \frac{2k_BT}{m\Gamma} t + \frac{2k_BT}{m\Gamma^2}(1 - e^{-\Gamma t})$$

we expand the exponential term to recover the leading order time dependence,

$$\langle x^2 \rangle = \frac{2k_BT}{m} t^2 \quad . \tag{15}$$

The mean square displacement in the short time is proportional to t^2 and is independent of the nature of the liquid. Or in other words, short dynamics is guided by inertial motion of the particle rather than any external influence.

C. Relation between random and viscous force : The fluctuation-dissipation theorem

We have the following Langevin equation

$$\frac{dv}{dt} = -\frac{6\pi\eta r v}{m} + \frac{1}{m}F(t) \tag{16}$$

where, the first and the second terms are due to viscous and random forces, respectively. We rewrite (16) after multiplying both sides by v [since $\Gamma = (6\pi\eta r)/m$]

$$v\frac{dv}{dt} = -\Gamma v^2 + \frac{1}{m} vF(t) \tag{17}$$

or

$$\frac{dv^2}{dt} = -2\Gamma v^2 + \frac{2}{m} vF(t) \quad .$$

Taking ensemble average we obtain

$$\frac{d}{dt}\langle v^2 \rangle = -2\Gamma \langle v^2 \rangle + \frac{2}{m}\langle vF(t) \rangle \quad . \tag{18}$$

The above equation requires the determination of $\langle vF(t) \rangle$; to this end we start from the identity

$$\int_{t-\Delta t}^{t} \dot{v}(t')\, dt' = v(t) - v(t-\Delta t) \tag{19}$$

or

$$v(t) = v(t-\Delta t) + \int_{t-\Delta t}^{t} \dot{v}(t')\, dt' \quad . \tag{20}$$

Multiplying both sides by $F(t)$ and taking average

$$\langle v(t)F(t)\rangle = \langle v(t-\Delta t)F(t)\rangle + \int_{t-\Delta t}^{t} \langle \dot{v}(t')F(t)\rangle\, dt' \quad . \tag{21}$$

The first term of the right hand side of Eq.(21) vanishes because of the velocity $v(t-\Delta t)$ at earlier instant $t-\Delta t < t$ has no dependence on the future fluctuating force $F(t)$. Thus,

$$\langle v(t-\Delta t)F(t)\rangle = 0 \quad .$$

Therefore

$$\langle v(t)F(t)\rangle = \int_{t-\Delta t}^{t} \langle \dot{v}(t')F(t)\rangle\, dt' \quad . \tag{22}$$

Putting the expression for $\dot{v}$ in above expression

$$\begin{aligned}
\langle v(t)F(t)\rangle &= \int_{t-\Delta t}^{t} \left\langle \left[-\Gamma v(t') + \frac{1}{m}F(t')\right] F(t) \right\rangle dt' \\
&= \int_{t-\Delta t}^{t} \Gamma \langle v(t')F(t)\rangle\, dt' + \int_{t-\Delta t}^{t} \frac{1}{m}\langle F(t')F(t)\rangle\, dt' \quad ,
\end{aligned} \tag{23}$$

the first term on the right hand side of Eq.(23) is zero again since t' is the earlier time ($< t$) and the fluctuating force at a later time t has no dependence on velocity earlier time t' except at $t = t'$ for which the integral is zero. We are left with

$$\langle v(t)F(t)\rangle = \frac{1}{m}\int_{t-\Delta t}^{t} \langle F(t')F(t)\rangle\, dt' \tag{24}$$

We now assume that $F(t)$, the fluctuating force, is stationary in time. This means the value of the integral (24) depends only on the difference $t - t'$ but not on t and t' individually[5]

$$\begin{aligned}
\langle v(t)F(t)\rangle &= \frac{1}{m}\int_{t-\Delta t}^{t} \langle F(t')F(t)\rangle\, dt' \\
&= \frac{1}{2m}\int_{t-\Delta t}^{t+\Delta t} \langle F(t')F(t)\rangle\, dt' \\
&= \frac{1}{2m}\int_{t-\Delta t}^{t+\Delta t} \langle F(t)F(t+s)\rangle\, ds \quad , \qquad t = t' + s \\
&= \frac{1}{2m}\int_{-\infty}^{+\infty} \langle F(0)F(s)\rangle\, ds
\end{aligned} \tag{25}$$

Here it is important to note that, (i) since $\Delta t \gg (t - t' = s)$, we put $\Delta t \sim \infty$ and (ii) The instant t is long (equilibrium time) and arbitrary so that we may put $t = 0$ without any loss of generality.

We now return to Eq.(18) and put the value of the $\langle v(t)F(t)\rangle$ from (25) to obtain

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[5]In general, the stationarity of a correlation function means that it is invariant under time translation, i.e., $\langle F(t)F(t')\rangle = \langle F(t+T)F(t'+T)\rangle$

$$\frac{d}{dt}\langle v^2\rangle = -2\Gamma\langle v^2\rangle + \frac{1}{m}\int_{-\infty}^{+\infty} ds\ \langle F(0)F(s)\rangle \tag{26}$$

In thermal equilibrium, the time derivative vanishes and the law of equipartition states

$$\frac{1}{2}m\langle v^2\rangle = \frac{1}{2}k_BT \tag{27}$$

Eq.(26) therefore gives,

$$0 = -2\Gamma\langle v^2\rangle + \frac{1}{m}\int_{-\infty}^{+\infty} ds\ \langle F(0)F(s)\rangle$$

Applying (27) we obtain

$$\Gamma = \frac{1}{2mk_BT}\int_{-\infty}^{+\infty} ds\ \langle F(0)F(s)\rangle \quad . \tag{28}$$

The above equation is known as the fluctuation-dissipation theorem, since it relates the dissipation Γ to the correlation of the fluctuating force $F(t)$. It expresses a balance between the input of energy flow into the system (particle) due to the fluctuating forces imparted by the liquid and the output of energy flow from the system due to dissipative forces exerted by the liquid on the system.

One can easily have a relation between the diffusion in velocity space and viscosity. For this purpose we require that the fluctuating forces $F(t)$ are instantaneously correlated, i.e., we use

$$\langle F(0)F(s)\rangle = 2\mathcal{D}\delta(s) \quad .$$

Also since, $\Gamma = (6\pi\eta r/m)$, we have from Eq.(28)

$$\frac{6\pi\eta r}{m} = \frac{\mathcal{D}}{mk_BT}\int_{-\infty}^{+\infty}\delta(s)ds$$

or

$$\mathcal{D} = 6\pi\eta r k_BT \quad .$$

Thus this relation may be visualized as special form of fluctuation-dissipation theorem.

III. BROWNIAN MOTION IN VELOCITY SPACE : FOKKER-PLANCK EQUATION

A. Fokker-Planck equation

In Einstein's method we considered the problem of Brownian motion in co-ordinate space, i.e., it concerns the time development of distribution of suspended particles in terms of $f(x,t)$, or the probability of finding a particle at the position x at a time t. The law of evolution was stated to be,

$$f(x, t+\tau) = \int_{-\infty}^{+\infty} f(x+\Delta, t)\ \phi(\Delta)\ d\Delta \tag{1}$$

where one takes into account of all the possible jumps of magnitude Δ from $x+\Delta$ to x, each with probability $\phi(\Delta)$. The differential form of the above equation is the diffusion equation,

$$\frac{\partial f(x,t)}{\partial t} = D\frac{\partial^2 f(x,t)}{\partial x^2} \tag{2}$$

where $D = \int_{-\infty}^{+\infty}\frac{\Delta^2}{2}\phi(\Delta)\ d\Delta$ is the diffusion coefficient in co-ordinate space.

Herein we approach the problem of Brownian motion in velocity space (as in Langevin description) and are concerned with the probability $f(v,t)$ that a particle has a velocity v at a time t. The technique is applicable to any fluctuating quantity. For the sake of simplicity we consider, however, the problem in one dimension.

The time development of probability distribution $f(v,t)$ of velocities may be stated as,

$$f(v,t+\tau) = \int_{-\infty}^{+\infty} f(v-\Delta,t)\ \phi(v-\Delta,\Delta)\ d\Delta \tag{3}$$

Here $\phi(v-\Delta,\Delta)$ is the probability of a jump Δ for a particle with velocity $v-\Delta$. Note that Δ has a dimension of velocity. Both τ and Δ are small such that higher power of them may be neglected in the calculation. We now expand $f(v,t+\tau)$ around t and $f(v-\Delta,t)\ \phi(v-\Delta,\Delta)$ around v such that

$$f(v,t+\tau) = f(v,t) + \tau\frac{\partial f}{\partial t} + \frac{\tau^2}{2}\frac{\partial^2 f}{\partial t^2} + \ldots \tag{4}$$

$$f(v-\Delta,t)\phi(v-\Delta,\Delta) = f(v,t)\phi(v,\Delta) - \Delta\frac{\partial(f\phi)}{\partial v} + \frac{\Delta^2}{2}\frac{\partial^2(f\phi)}{\partial v^2} \tag{5}$$

Putting (4) and (5) in (3) we obtain,

$$\begin{aligned}
f(v,t) + \tau\frac{\partial f}{\partial t} + \mathcal{O}(\tau^2) &= \int_{-\infty}^{+\infty} \left[f(v,t)\phi(v,\Delta) - \Delta\frac{\partial(f\phi)}{\partial v} + \frac{\Delta^2}{2}\frac{\partial^2(f\phi)}{\partial v^2}\right]\ d\Delta \\
&= f(v,t)\int_{-\infty}^{+\infty} \phi(v,\Delta)\ d\Delta - \frac{\partial}{\partial v}\left[f(v,t)\int_{-\infty}^{+\infty} \Delta\ \phi(v,\Delta)\ d\Delta\right] \\
&\quad + \frac{\partial^2}{\partial v^2}\left[f(v,t)\int_{-\infty}^{+\infty} \frac{\Delta^2}{2}\phi(\Delta,v)\ d\Delta\right]
\end{aligned} \tag{6}$$

Note that $\int_{-\infty}^{+\infty} \phi(v,\Delta)\ d\Delta = 1$ [probability is normalized]. We then write,

$$\begin{aligned}
\frac{1}{\tau}\int_{-\infty}^{+\infty} \Delta\ \phi(v,\Delta)\ d\Delta = \frac{\langle\Delta(v)\rangle}{\tau} &= M_1(v) \\
\frac{1}{\tau}\int_{-\infty}^{+\infty} \frac{\Delta^2}{2}\ \phi(v,\Delta)\ d\Delta = \frac{\langle\Delta^2(v)\rangle}{\tau} &= M_2(v)
\end{aligned}$$

Eq.(6) can be rewritten as,

$$\frac{\partial f(v,t)}{\partial t} = -\frac{\partial}{\partial v}M_1(v)\ f(v,t) + \frac{\partial^2}{\partial v^2}M_2(v)\ f(v,t) \tag{7}$$

$M_1(v)$ and $M_2(v)$ are called the drift and diffusion terms, respectively. Eq.(7) is called the Fokker-Planck equation. M_2 is the diffusion in velocity space and is not to be confused with$D$ of Eq.(2) in co-ordinate space.

For complete specification of Fokker-Planck equation one therefore needs the information about the drift, $M_1(v)$ and diffusion, $M_2(v)$ terms in Eq.(7). We calculate here these quantities for a specific model, i.e., the Brownian motion.

B. Calculation of $M_1(v)$

We integrate the Langevin equation

$$\frac{dv}{dt} = -\alpha v + F(t) \tag{8}$$

between t and $t+\tau$ to obtain

$$v(t+\tau) - v(t) = -\alpha v\tau + \int_t^{t+\tau} F(t')\ dt' \tag{9}$$

α in Eq.(8) is the dissipation or damping constant and $F(t)$ is the random force whose average is zero, i.e., $\langle F(t)\rangle = 0$. We now put $\Delta = v(t+\tau) - v(t)$, therefore,

$$\langle v(t+\tau) - v(t)\rangle = \langle \Delta \rangle = -\alpha v \tau$$

or

$$M_1(v) = \frac{\langle \Delta \rangle}{\tau} = -\alpha v \tag{10}$$

is the drift term.

C. Calculation of $M_2(v)$

From Eq.(9) we write

$$\Delta^2 = \alpha^2 v^2 \tau^2 - 2\alpha v \tau \int_t^{t+\tau} F(t')\, dt' + G_t^2(\tau) \tag{11}$$

where $G_t(\tau) = \int_t^{t+\tau} F(t')\, dt'$. Since τ is very small, the first term is neglected. Also the second term by virtue of $\langle F(t)\rangle = 0$ is zero. So we are left with (after averaging)

$$\langle \Delta^2 \rangle = \langle G_t^2(\tau) \rangle$$

$$\langle \Delta^2 \rangle = \int_t^{t+\tau} dt' \int_t^{t+\tau} \langle F(t')F(t'')\rangle\, dt'' \tag{12}$$

If we assume that the random force is instantaneously correlated, i.e.,

$$\langle F(t')F(t'')\rangle = 2\mathcal{D}\delta(t' - t'')$$

we obtain the average of Δ^2 as

$$\begin{aligned}\langle \Delta^2 \rangle &= 2\mathcal{D} \int_t^{t+\tau} dt' \int_t^{t+\tau} \delta(t' - t'')\, dt'' \\ &= 2\mathcal{D} \int_t^{t+\tau} dt'\end{aligned}$$

or

$$\langle \Delta^2 \rangle = 2\mathcal{D}\tau \tag{13}$$

Therefore, $M_2(v) = \frac{\langle \Delta^2 \rangle}{2\tau} = \mathcal{D}$, the diffusion constant in velocity space, which is to be determined for the model represented by Eq.(8).

To determine $\mathcal{D}$ we first integrate Eq.(8) formally with the integrating factor $e^{-\alpha t}$ and obtain

$$v(t) = v(0)e^{-\alpha t} + e^{-\alpha t} \int_0^t e^{-\alpha t'} F(t')\, dt' \tag{14}$$

Rearranging and taking the square on both sides we have

$$(v(t) - v(0)e^{-\alpha t})^2 = e^{-2\alpha t} \int_0^t dt' \int_0^t e^{\alpha(t'+t'')} F(t')F(t'')\, dt'' \tag{15}$$

Averaging yields

$$\langle (v(t) - v(0)e^{-\alpha t})^2 \rangle = e^{-2\alpha t} \int_0^t dt' \int_0^t e^{\alpha(t'+t'')} \langle F(t')F(t'')\rangle\, dt'' \tag{16}$$

Putting $\langle F(t')F(t'')\rangle = 2\mathcal{D}\delta(t' - t'')$ in (16) we obtain

$$\langle (v(t) - v(0)e^{-\alpha t})^2 \rangle = 2e^{-2\alpha t}\mathcal{D}\int_0^t dt' e^{2\alpha t'} \tag{17}$$

Explicit integration in the last equation yields

$$\begin{aligned}\langle (v(t) - v(0)e^{-\alpha t})^2 \rangle &= 2e^{-2\alpha t}\mathcal{D}\left[\frac{e^{2\alpha t} - 1}{2\alpha}\right] \\ &= \frac{\mathcal{D}}{\alpha}(1 - e^{-2\alpha t})\end{aligned}$$

For $t \gg 1/\alpha$, we have

$$\langle v(t)^2 \rangle = \frac{\mathcal{D}}{\alpha} \quad . \tag{18}$$

The above relation together with the equipartition theorem $\frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}k_B T$ leads us to

$$\mathcal{D} = \alpha k_B T/m \tag{19}$$

Thus $M_2(v) = \mathcal{D} = \alpha k_B T/m$, (diffusion coefficient in velocity space).

The above $\mathcal{D}$ is not to be confused D of Eq.(22) which is a diffusion coefficient for the Brownian particle in co-ordinate space.

With these M_1 and M_2 the Fokker-Planck equation for the Brownian motion can be rewritten as

$$\frac{\partial f(v,t)}{\partial t} = \frac{\partial}{\partial v}[\alpha v]f(v,t) + \frac{\partial^2}{\partial v^2}\left[\frac{\alpha k_B T}{m}\right]f(v,t) \tag{20}$$

Putting $p = mv$ the above equation (20) can be rewritten in the momentum space as follows

$$\frac{\partial P(p,t)}{\partial t} = \frac{\partial}{\partial p}[\alpha p]P(p,t) + \frac{\partial^2}{\partial p^2}\left[\frac{\alpha k_B T}{m}\right]P(p,t) \tag{21}$$

where $f(v,t) \equiv P(p,t)$ represents the probability distribution function in momentum space. Here the underlying stochastic process is called the Ornstein-Uhlenbeck process (1930).

IV. BROWNIAN MOTION IN PHASE SPACE (MOTION IN A FORCE FIELD)

A. Kramers' equation

We first derive here the equation of diffusion for an ensemble of particles with probability density distribution $f(p,q,t)$ in phase space (i.e., q, p-space). The evolution of distribution from the time t to another time $t + \tau$ is given by the following equation,

$$f(p_1, q_1, t + \tau) = \int_{-\infty}^{+\infty} f(p - \Delta, q, t)\phi(p - \Delta, q, \Delta)d\Delta \tag{1}$$

Had there been no Brownian motion, the motion would have been purely deterministic, i.e.,

$$\left.\begin{aligned}\dot{q} &= p, \\ \dot{p} &= \mathcal{K}(q)\end{aligned}\right\} \tag{2}$$

where $\mathcal{K}(q)$ is the force acting on the particles. Thus the time development of q and p over a small time τ would be

$$q_1 = q + p\tau \;\text{ and }\; p_1 = p + \mathcal{K}\tau \quad . \tag{3}$$

Here (q,p) and (q_1,p_1) specify the co-ordinate-momentum pair at time t and $t + \tau$.

Because the particle is also subjected to a random Brownian force, we account for the all the possible jumps (of magnitude Δ) in momentum with the probability function $\phi(p - \Delta, q, \Delta)$ and an integration over Δ in Eq.(1).

Making use of Eq.(3) we rewrite Eq.(1) as,

$$f(p+\mathcal{K}\tau, q+p\tau, t+\tau) = \int_{-\infty}^{+\infty} f(p-\Delta, q, t)\phi(p-\Delta, q, \Delta)d\Delta \tag{4}$$

We now expand $f(p+\mathcal{K}\tau, q+p\tau, t+\tau)$ in a Taylor series as,

$$f(p,q,t) + \frac{\partial f}{\partial p}\mathcal{K}\tau + \frac{\partial f}{\partial q}p\tau + \frac{\partial f}{\partial t}\tau + \ldots \tag{5}$$

Also expanding $f(p-\Delta, q, t)\phi(p-\Delta, q, \Delta)$ as,

$$f(p,q,t)\phi(p,q,\Delta) - \frac{\partial(f\phi)}{\partial p}\Delta + \frac{1}{2!}\frac{\partial^2(f\phi)}{\partial p^2}\Delta^2 + \ldots \tag{6}$$

Integration over Δ in Eq.(6) gives

$$\int_{-\infty}^{+\infty} f(p-\Delta, q, t)\phi(p-\Delta, q, \Delta)d\Delta$$

$$= f\int_{-\infty}^{+\infty}\phi(p,q,\Delta)d\Delta - \frac{\partial}{\partial p}[f]\int_{-\infty}^{+\infty}\Delta\phi(p,q,\Delta)d\Delta + \frac{\partial^2}{\partial p^2}[f]\int_{-\infty}^{+\infty}\frac{\Delta^2}{2}\phi(p,q,\Delta)d\Delta$$

$$= f(p,q,t) - \frac{\partial}{\partial p}[f(p,q,t)M_1(p,q)] + \frac{\partial^2}{\partial p^2}[f(p,q,t)M_2(p,q)] \ . \tag{7}$$

We now put

$$\begin{aligned}
\textstyle\int_{-\infty}^{+\infty}\phi(p,q,\Delta)d\Delta &= 1 \\
\textstyle\int_{-\infty}^{+\infty}\Delta\phi(p,q,\Delta)d\Delta &= \overline{\Delta} \\
\textstyle\int_{-\infty}^{+\infty}\frac{\Delta^2}{2}\phi(p,q,\Delta)d\Delta &= \overline{\Delta^2}/2
\end{aligned}$$

Using Eq.(5) and Eq.(7) in Eq.(4) we obtain

$$\frac{\partial f}{\partial p}\mathcal{K}\tau + \frac{\partial f}{\partial q}p\tau + \frac{\partial f}{\partial t}\tau = -\frac{\partial}{\partial p}[f\overline{\Delta}] + \frac{\partial^2}{\partial p^2}[f\overline{\Delta^2}] \tag{8}$$

Dividing both sides of Eq.(8) by τ we get

$$\frac{\partial f}{\partial p}\mathcal{K} + \frac{\partial f}{\partial q} + \frac{\partial f}{\partial t} = -\frac{\partial}{\partial p}(fM_1) + \frac{\partial^2}{\partial p^2}(fM_2) \tag{9}$$

where $M_1 = \overline{\Delta}/\tau$ and $M_2 = \overline{\Delta^2}/2\tau$. Thus rearranging Eq.(9) we write

$$\frac{\partial f}{\partial t} = -p\frac{\partial f}{\partial q} - \mathcal{K}(q)\frac{\partial f}{\partial p} - \frac{\partial}{\partial p}[M_1(p,q)f] + \frac{\partial^2}{\partial p^2}[M_2(p,q)f] \ . \tag{10}$$

Since the force $\mathcal{K}(q)$ is derivable from a potential $V(q)$ we write

$$\mathcal{K}(q) = -V'(q) \tag{11}$$

From the knowledge of Brownian motion (as calculated in the last section) we know,

$$\left.\begin{aligned} M_1 &= -\gamma p = -m\gamma v \\ M_2 &= \mathcal{D} = m\gamma k_B T \end{aligned}\right\} \tag{12}$$

Take the mass of the particle $m = 1$ for simplicity. Then writing $q = x$ and $p = v$ Eq.(10) reduces to

$$\frac{\partial f}{\partial t} = -\frac{\partial f}{\partial x}v + \frac{\partial f}{\partial v}[V'(x)] + \frac{\partial}{\partial v}[\gamma v]f + \gamma k_B T\frac{\partial^2 f}{\partial v^2} \tag{13}$$

The above equation is called the Kramers' equation [6,7]. It describes the Brownian motion of a particle which is in a field of force. Or in other words a particle moves in an external field but in addition is subjected to irregular forces (at the same time) of the surrounding medium. While the first two terms are due to the deterministic motion, the third and the fourth terms are the drift and diffusion terms which are characteristic of Brownian motion.

B. Kramers equation as a generalization of Liouville equation and connection to equilibrium statistical mechanics

The deterministic motion described by (13), i.e.,

$$\frac{\partial f(x,v,t)}{\partial t} = -\frac{\partial f}{\partial x}v + \frac{\partial f}{\partial v}[V'(x)] \tag{14}$$

corresponds to Liouville equation which forms the basis of equilibrium statistical mechanics under the condition $\frac{\partial f}{\partial t} = 0$ (which defines the equilibrium)

It is now wellknown that under equilibrium condition the distribution is a Maxwell-Boltzmann distribution, i.e., (we assume $m = 1$)

$$f(x,v) = Z\, e^{-\frac{\frac{1}{2}v^2 + V(x)}{k_B T}} \tag{15}$$

where Z is the normalization constant. Thus (15) satisfies (14) for $\frac{\partial f}{\partial t} = 0$ as may be checked.

It is important to emphasize that if we keep the Brownian dynamical terms in (13) as such and put the equilibrium condition $\frac{\partial f}{\partial t} = 0$ then it may also be checked that (15) satisfies (13) under the equilibrium condition $\frac{\partial f}{\partial t} = 0$.

Kramers' equation may thus be regarded as a generalization of Liouville equation since it includes the Brownian motion in such a way that the basis of equilibrium statistical mechanics remains unaffected.

C. Kramers' theory of activated processes

Kramers' model for a chemical reaction consists of a classical particle of mass m (considered here to be unity) moving in a one-dimensional asymmetric double-well potential $V(x)$. The particles co-ordinate x corresponds to the reaction co-ordinate and its value at the minima of the potential $V(x)$, x_a and x_c denotes the reactant and the product states, respectively. The maximum of $V(x)$ at $x = x_b$ separating these states corresponds to the transition state (or activated complex). All the remaining degrees of freedom of reactants and the solvent molecules constitute the surrounding medium whose total effect on the reacting particle is described by a fluctuating force and a linear damping. The correlation of fluctuating force gives rise to diffusion coefficient and the linear damping is responsible for the drift term. The stochastic dynamics for the reaction co-ordinate x and velocity v is governed by Kramers' equation [6]

$$\frac{\partial}{\partial t}P(x,v,t) = \left[-\frac{\partial}{\partial x}v + \frac{\partial}{\partial v}\left\{V'(x) + \gamma v\right\} + \gamma k_B T\frac{\partial^2}{\partial v^2}\right]P(x,v,t) \tag{1}$$

The conditions are such that the particle is originally caught in the left well may escape in the course of time due to thermal activation by passing over the potential barrier. We want to calculate the probability of escape and its dependency on temperature and viscosity of the medium and compare the value with the result of 'transition state method'. The calculation rests on the equation of diffusion obeyed by a density-distribution of particles in phase space as written above [Eq. (1)].

To determine the steady state escape rate from A to C (say) we consider that there is a stationary situation in which a steady state probability current (flux) over B from A→C is maintained.

The stationary probability density must satisfy the following conditions :

• Since we are considering a stationary situation, i.e., $\frac{\partial P}{\partial t} = 0$ we write,

$$\left[-\frac{\partial}{\partial x}v + \frac{\partial}{\partial v}\left\{V'(x) + \gamma v\right\} + \gamma k_B T\frac{\partial^2}{\partial v^2}\right]P(x,v) = 0 \tag{2}$$

•• At the barrier top B we assume the linearized potential, i.e., we write by expanding $V(x)$ around x_b

$$V(x) = V(x_b) + \left.\frac{\partial V}{\partial x}\right|_{x=x_b}(x - x_b) + \frac{1}{2}\left.\frac{\partial^2 V}{\partial x^2}\right|_{x=x_b}(x - x_b)^2$$

---

[6]here we have put $f(x,v,t) = P(x,v,t)$; just a change in notation

Since $\frac{\partial V}{\partial x}\Big|_{x=x_b} = 0$ and $-\left.\frac{\partial^2 V}{\partial x^2}\right|_{x=x_b} = \omega_b^2$ we have,

$$V(x) = V(x_b) - \frac{1}{2}\omega_b^2(x - x_b)^2 \quad . \tag{3}$$

While considering the motion around $x = x_b$ the above potential (3) has to be used in Eq.(2).

• • • Near the bottom of the A-well all the particles are thermalized. Therefore we must have the usual Boltzmann distribution to be valid here, i.e. ,

$$P(x, v) = z^{-1} \exp\left[\left\{-\frac{1}{2}v^2 + V(x)\right\}/k_B T\right] \quad \text{at } x \approx x_a \tag{4}$$

The linearization of potential has to be done at $x = x_a$, i.e., we write

$$V(x) = V(x_a) + \left.\frac{\partial V}{\partial x}\right|_{x=x_a}(x - x_a) + \frac{1}{2}\left.\frac{\partial^2 V}{\partial x^2}\right|_{x=x_a}(x - x_a)^2$$

Since $\frac{\partial V}{\partial x}\Big|_{x=x_a} = 0$ and $-\left.\frac{\partial^2 V}{\partial x^2}\right|_{x=x_a} = \omega_a^2$ we have,

$$V(x) = V(x_a) + \frac{1}{2}\omega_a^2(x - x_a)^2 \quad . \tag{5}$$

While considering the motion around $x = x_a$, the potential $V(x)$ as given by Eq.(5) has to be used in Eq.(2)

• • •• Near the bottom of the well C all the particles are (as if) removed. This implies the condition

$$P(x, v) \sim 0 \quad \text{for } x > x_b \quad . \tag{6}$$

Once the probability density $P(x, v)$ fulfilling the above requirements is known, the population in the A-well n_a and the flux j over the barrier will be given by

$$n_a = \int_{\text{Awell}} dx\, dv\, P(x, v) \tag{7}$$

$$j = \int_{-\infty}^{+\infty} dv\, v\, P(x, v) \tag{8}$$

Hence the steady state Kramers' rate is given by

$$k_{A\to C} = j/n_a \quad . \tag{9}$$

Our next task is to calculate j and n_a separately.

1. Calculation of j

Since we are considering the flux over the barrier B, the linearized potential $V(x) = V(x_b) - \frac{1}{2}\omega_b^2(x - x_b)^2$ has to be used. The Kramers' equation[7] therefore reduces to

$$\left[-v\frac{\partial}{\partial x} + \frac{\partial}{\partial v}\left\{-\omega_b^2(x - x_b) + \gamma v\right\} + \gamma k_B T\frac{\partial^2}{\partial v^2}\right] P(x, v) = 0 \quad . \tag{10}$$

We now construct $P(x, v)$ in the following form

$$P(x, v) = \xi(x, v) \exp\left[\frac{-\frac{1}{2}v^2 + V(x)}{k_B T}\right] \quad , \quad x \approx x_b \quad . \tag{11}$$

[7]since $V'(x) = -\omega_b^2(x - x_b)$

Putting Eq.(11) in Eq.(10) we get after a little bit of straightforward algebra

$$\left[-v\frac{\partial}{\partial x} - \left\{\omega_b^2(x-x_b) + \gamma v\right\}\frac{\partial}{\partial v} + \gamma k_B T\frac{\partial^2}{\partial v^2}\right]\xi(x,v) = 0 \quad . \tag{12}$$

Boundary condition for $\xi(x,v)$ in Eq.(11) should be such that
- $\xi(x,v) \to 1$ inside the well A, for $x \approx x_a$.
- $\xi(x,v) \to 0$ beyond the barrier top B, for $x > x_b$.

We now use the following linear transformation

$$u = v \;+\; a(x - x_b) \tag{13}$$

where a is a constant to be determined later. This gives

$$\left.\begin{array}{rcl} \frac{\partial}{\partial x} & = & a\frac{\partial}{\partial u} \\ \frac{\partial}{\partial v} & = & \frac{\partial}{\partial u} \end{array}\right\} \tag{14}$$

Making use of Eq.(13) and Eq.(14) we obtain from Eq.(12)

$$-\,av\frac{\partial \xi}{\partial u} - \left[\omega_b^2(x-x_b) + \gamma v\right]\frac{\partial \xi}{\partial u} + \gamma k_B T\frac{\partial^2 \xi}{\partial u^2} = 0 \tag{15}$$

or

$$\gamma k_B T\frac{\partial^2 \xi}{\partial u^2} - \left[\omega_b^2(x-x_b) + v(a+\gamma)\right]\frac{\partial \xi}{\partial u} = 0 \tag{16}$$

We now put :

$$\omega_b^2(x-x_b) + v(a+\gamma) = -\lambda u \;\;,\;\; \lambda = \text{constant (to be determined).}$$

Since

$$u = v \;+\; a(x - x_b)$$

we have,

$$\omega_b^2(x-x_b) \;+\; v(a+\gamma) = -\lambda[v + a(x-x_b)] \;\; .$$

Comparing both sides

$$\left.\begin{array}{rcl} -\lambda a & = & \omega_b^2 \\ -\lambda & = & a+\gamma \end{array}\right\} \tag{17}$$

From Eq.(17) we eliminate λ to obtain

$$a^2 + \gamma a - \omega_b^2 = 0$$

which gives

$$a = -\frac{\gamma}{2} \pm \sqrt{\left(\frac{\gamma}{2}\right)^2 + \omega_b^2} \tag{18}$$

and

$$\lambda = -\omega_b^2/a \;\; .$$

Eq.(16) now reduces to

$$\gamma k_B T\frac{\partial^2 \xi}{\partial u^2} + \lambda u\frac{\partial \xi}{\partial u} = 0 \tag{19}$$

or

$$\frac{\partial^2 \xi}{\partial u^2} + \frac{\lambda u}{\gamma k_B T}\frac{\partial \xi}{\partial u} = 0 \tag{20}$$

Our next task is to solve Eq.(20). We put $\frac{\partial \xi}{\partial u} = y$. Therefore Eq.(20) reduces to

$$\frac{\partial y}{\partial u} = -\frac{\lambda}{\gamma k_B T} u y \tag{21}$$

Integrating over u Eq.(21) gives

$$\ln y = -\frac{\lambda}{\gamma k_B T} u^2 + \ln F_2 \quad , \quad F_2 = \text{constant of integration}$$

$$y = F_2 \; \exp\left(-\frac{\lambda u^2}{2\gamma k_B T}\right)$$

Since

$$\frac{\partial \xi}{\partial u} = y = F_2 \; \exp\left(-\frac{\lambda u^2}{2\gamma k_B T}\right)$$

we get

$$\xi(u) = F_2 \int_0^u \exp\left(-\frac{\lambda u^2}{2\gamma k_B T}\right) + F_1 \quad , \quad F_1 = \text{constant of integration} \tag{22}$$

We look for a solution that vanishes at $x \to \infty$; the above integral should however remain finite for all $|u| \to \infty$. This implies $\lambda > 0$, i.e., positive. Since

$$\lambda = -\omega_b^2 / a \tag{23}$$

the negative root of a should be chosen to keep λ positive, i.e.,

$$a = -\frac{\gamma}{2} - \sqrt{\left(\frac{\gamma}{2}\right)^2 + \omega_b^2} \; . \tag{24}$$

Thus λ and a are known in terms of the given parameters γ and ω_b^2 of the problem.

Next we determine F_1 and F_2 (the integration constants).

When $x \to \infty$ then $u \to -\infty$, since $u = v + a(x - x_b)$ and a is negative. Again when $x \to \infty$ we must have $\xi(x, v) \to 0$. Therefore from Eq.(22) we obtain

$$0 = F_1 + F_2 \int_0^{-\infty} \exp\left(-\frac{\lambda u^2}{2\gamma k_B T}\right) \, du$$

or

$$\begin{aligned}
F_1 &= F_2 \int_{-\infty}^{0} \exp\left(-\frac{\lambda u^2}{2\gamma k_B T}\right) \, du \\
F_1 &= F_2 \, \frac{1}{2} \int_{-\infty}^{+\infty} \exp\left(-\frac{\lambda u^2}{2\gamma k_B T}\right) \, du \\
F_1 &= F_2 \sqrt{\frac{\pi \gamma k_B T}{2\lambda}}
\end{aligned} \tag{25}$$

Therefore we obtain

$$\xi(u) = F_2 \left[\sqrt{\frac{\pi \gamma k_B T}{2\lambda}} + \int_0^u \exp\left(-\frac{\lambda u^2}{2\gamma k_B T}\right) \, du\right] \; . \tag{26}$$

We then return to the expression for $P(x, v)$

$$P(x,v) = \xi(x,v) \exp\left[-\frac{\frac{1}{2}v^2 + V(x_b) - \frac{1}{2}\omega_b^2(x-x_b)^2}{k_BT}\right] \ , \ x \approx x_b \ . \tag{27}$$

Using Eq.(26) we get from Eq.(27)

$$\begin{aligned} P(x,v) = F_2 \ & \left[\sqrt{\frac{\pi\gamma k_BT}{2\lambda}} + \int_0^u \exp\left(-\frac{\lambda u^2}{2\gamma k_BT}\right) \ du\right] \\ & \times \exp\left[-\frac{\frac{1}{2}v^2 + V(x_b) - \frac{1}{2}\omega_b^2(x-x_b)^2}{k_BT}\right] \ . \end{aligned} \tag{28}$$

Writing

$$C = \sqrt{\frac{\pi\gamma k_BT}{2\lambda}}$$

and

$$F(x,v) = \int_0^u \exp\left(-\frac{\lambda u^2}{2\gamma k_BT}\right) \ du$$

Eq.(28) reduces to

$$\begin{aligned} P(x_b,v) = F_2 \ \exp\left(-\frac{V(x_b)}{k_BT}\right) \\ \times \left[C \ \exp\left(-\frac{1}{2}v^2/k_BT\right) \ + \ F(x_b,v) \ \exp\left(-\frac{1}{2}v^2/k_BT\right)\right] \ , \ x \approx x_b \end{aligned} \tag{29}$$

The expression for the current j is given by

$$j = \int_{-\infty}^{+\infty} v \ P(x_b,v) \ dv \tag{30}$$

Since the first term in Eq.(29) can not contribute to Eq.(30) because of

$$\int_{-\infty}^{+\infty} ve^{-\frac{1}{2}v^2/k_BT} dv = 0$$

we write

$$\begin{aligned} j &= F_2 \ e^{-\frac{V(x_b)}{k_BT}} \left[\int_{-\infty}^{+\infty} v \ e^{-v^2/2k_BT} \ F(x_b,v) \ dv\right] \\ &= F_2 \ e^{-\frac{V(x_b)}{k_BT}} \ (-k_BT) \int_{-\infty}^{+\infty} \frac{\partial}{\partial v} \ e^{-v^2/2k_BT} \ F(x_b,v) \ dv \\ &= F_2 \ e^{-\frac{V(x_b)}{k_BT}} \ (-k_BT) \ \left\{ F(x,v)e^{-v^2/2k_BT}\Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \frac{\partial F}{\partial v} \ e^{-v^2/2k_BT} \ dv \right\} \\ &= F_2 \ e^{-\frac{V(x_b)}{k_BT}} \ (k_BT) \ \int_{-\infty}^{+\infty} \frac{\partial F}{\partial v} \ e^{-v^2/2k_BT} \ dv \end{aligned} \tag{31}$$

Since[8]

$$\begin{aligned} F(x,v) &= \int_0^u \exp\left(-\frac{\lambda u^2}{2\gamma k_BT}\right) \ du \\ \frac{\partial F}{\partial v} &= \exp\left(-\frac{\lambda v^2}{2\gamma k_BT}\right) \ . \end{aligned}$$

[8]since at $x = x_b$ $u = v$

Therefore Eq.(28) gives

$$j = F_2\, e^{-\frac{V(x_b)}{k_BT}}\ k_BT \int_{-\infty}^{+\infty} e^{-\frac{\lambda v^2}{2\gamma k_BT}}\ e^{-\frac{v^2}{2k_BT}}\ dv \tag{32}$$

$$= F_2\, e^{-\frac{V(x_b)}{k_BT}}\ k_BT \int_{-\infty}^{+\infty} e^{-\left[\frac{\lambda}{2\gamma k_BT}+\frac{1}{2k_BT}\right]v^2}\ dv \tag{33}$$

$$= F_2\, e^{-\frac{V(x_b)}{k_BT}}\ (k_BT)\ (2\pi k_BT)^{1/2} \left(\frac{\gamma}{\lambda+\gamma}\right)^{1/2} \quad . \tag{34}$$

Finally we get the expression for steady state current

$$j = F_2\, e^{-\frac{V(x_b)}{k_BT}}\ (2\pi)^{1/2}\ (k_BT)^{3/2} \left(\frac{\gamma}{\lambda+\gamma}\right)^{1/2} \tag{35}$$

2. Calculation of n_a

The number of particles in the left well A is given by

$$n_a = \int_{-\infty}^{+\infty} dv \int_{-\infty}^{+\infty} dx\ P(x,v) \tag{36}$$

Since $P(x,v)$ is given by

$$P(x,v) = \xi(x,v)\ \exp\left[-\frac{\frac{1}{2}v^2 + V(x)}{k_BT}\right]$$

and $\xi(x,v)$ is obtained from Eq.(26). Thus

$$P(x,v) = F_2 \left[\left(\frac{\pi\gamma k_BT}{2\lambda}\right)^{1/2} + \int_0^u e^{-\frac{\lambda u^2}{2\gamma k_BT}}\ du\right] e^{-\frac{\frac{1}{2}v^2+V(x)}{k_BT}}$$

We have the following condition :

- As $x \to -\infty$, i.e., the left well ; $u \to \infty$ [since $u = v + a(x - x_b)$ and a is negative]. Therefore

$$\int_0^{\infty} e^{-\frac{\lambda u^2}{2\gamma k_BT}}\ du = \sqrt{\frac{2\pi k_BT\gamma}{2\lambda}}$$

$$P(x,v) = F_2 \left[\left(\frac{2\pi\gamma k_BT}{\lambda}\right)^{1/2}\right] e^{-\frac{\frac{1}{2}v^2+V(x)}{k_BT}} \quad .$$

Since

$$V(x) = V(x_a) + \frac{1}{2}\omega_a^2(x - x_a)^2$$

$$n_a = F_2 \left(\frac{2\pi\gamma k_BT}{\lambda}\right)^{1/2} e^{-\frac{V(x_a)}{k_BT}} \int_{-\infty}^{+\infty} e^{-\frac{v^2}{2k_BT}}\ dv \int_{-\infty}^{+\infty} e^{-\frac{\omega_a^2(x-x_a)^2}{2k_BT}}\ dx$$

$$= F_2 \left(\frac{2\pi\gamma k_BT}{\lambda}\right)^{1/2} e^{-\frac{V(x_a)}{k_BT}}\ (2\pi k_BT)^{1/2} \left(\frac{2\pi k_BT}{\omega_a^2}\right)^{1/2}$$

$$= F_2\ \frac{(2\pi k_BT)^{3/2}}{\omega_a} \left(\frac{\gamma}{\lambda}\right)^{1/2} e^{-\frac{V_a}{k_BT}} \quad . \tag{37}$$

We are now in a position to calculate the Kramers' rate

$$k = j/n_a \quad .$$

From Eq.(34) and Eq.(36) we get

$$k = \frac{F_2\ (k_B T)^{3/2}\ (2\pi)^{1/2}\ \left(\frac{\gamma}{\lambda+\gamma}\right)^{1/2}\ e^{-\frac{V(x_b)}{k_B T}}}{F_2\ \frac{(2\pi k_B T)^{3/2}}{\omega_a}\ \left(\frac{\gamma}{\lambda}\right)^{1/2}\ e^{-\frac{V(x_a)}{k_B T}}} \tag{38}$$

$$k = \frac{\omega_a}{2\pi}\ \left(\frac{\lambda}{\lambda+\gamma}\right)^{1/2}\ e^{-\frac{V(x_b)-V(x_a)}{k_B T}} \tag{39}$$

where $V(x_b) - V(x_a) = E$, the energy of activation. The pre-exponential factor in Eq.(35) can be simplified further as follows,

Since $\gamma + \lambda = a_-$ (negative root of a is a_-) [see Eq.(17)]

$$\begin{aligned} \lambda &= -(\gamma + a_-) \\ &= -\left[\gamma + \left\{-\frac{\gamma}{2} - \sqrt{\left(\frac{\gamma}{2}\right)^2 + \omega_b^2}\right\}\right] \\ &= -\frac{\gamma}{2} + \sqrt{\left(\frac{\gamma}{2}\right)^2 + \omega_b^2} \\ &= a_+ \ \text{(positive root of } a) \end{aligned}$$

$$\frac{\lambda}{\lambda+\gamma} = -\left(\frac{a_+}{a_-}\right) = -\frac{a_+ a_+}{a_- a_+} = \frac{\left(-\frac{\gamma}{2} + \sqrt{\left(\frac{\gamma}{2}\right)^2 + \omega_b^2}\right)^2}{\omega_b^2}$$

We thus get the final expression for Kramers' rate for arbitrary γ

$$k = \frac{\omega_a}{2\pi\omega_b}\ \left[-\frac{\gamma}{2} + \sqrt{\left(\frac{\gamma}{2}\right)^2 + \omega_b^2}\right]\ e^{-E/k_B T} \quad . \tag{40}$$

We now consider the two limiting cases in the above equation :

• when $\gamma \to 0$ (i.e., for small viscosity coefficient)

$$k_{\gamma\to 0} = \frac{\omega_a}{2\pi}\ e^{-E/k_B T} \tag{41}$$

which is the transition state result (independent of γ).

•• when $\gamma \to$ large, i.e., $\gamma \gg \omega_b$ (large viscosity limit)

$$\begin{aligned} k_{\gamma\to\text{large}} &= \frac{\omega_a}{2\pi\omega_b}\ \left[\frac{\gamma}{2}\ \left\{1 + \frac{1}{2}\ \frac{4\omega_b^2}{\gamma^2}\right\} - \frac{\gamma}{2}\right]\ e^{-E/k_B T} \\ &= \frac{\omega_a}{2\pi\omega_b}\ \frac{\omega_b^2}{\gamma}\ e^{-E/k_B T} \end{aligned}$$

or

$$k_{\gamma\to\text{large}} = \frac{\omega_a\omega_b}{2\pi\gamma}\ e^{-E/k_B T} \tag{42}$$

The rate of reaction is inversely proportional to the viscosity. This observation has been corroborated by a number of experimental investigations in the recent past.

The general result (39) which is valid in the intermediate to the strong damping limit provides a theoretical basis for Arrhenius expression for reaction rate $k = Ae^{-E/k_B T}$ proposed many years ago.

D. A simple connection to Transition State Theory

We start from Kramers' equation which describes the motion of a particle in a force field governed by the potential $V(x)$ simultaneously subjected to Brownian motion :

$$\frac{\partial}{\partial t}P(x,v,t) = \left[-\frac{\partial}{\partial x}v + \frac{\partial}{\partial v}\{V'(x) + \gamma v\} + \gamma k_B T\frac{\partial^2}{\partial v^2}\right] P(x,v,t)$$

We have shown that the equilibrium distribution $P_{eq}(x,v)$ corresponding to above equation is given by

$$P_{eq}(x,v) = Z\, e^{-\frac{\frac{1}{2}v^2+V(x)}{k_B T}}$$

One assumes a that the particles initially residing in the left well are equilibrated and also that the above distribution is valid for all x (around the bottom of the left well) except at the barrier top $x = B$. We therefore put

$$P_{eq}(x,v) = 0 \quad \text{for } \ x > B$$

The normalization constant Z is thus determined by the condition

$$\int_{-\infty}^{+\infty} dv \int_{-\infty}^{B} P_{eq}(x,v)\; dx = 1$$

$$\text{or,} \quad Z\int_{-\infty}^{+\infty} e^{-\frac{\frac{1}{2}v^2}{k_B T}}\; dv \int_{-\infty}^{B} P_{eq}(x,v)\; e^{-\frac{V(x)}{k_B T}}\; dx = 1$$

$$Z\,\sqrt{2\pi k_B T}\;\int_{-\infty}^{B} e^{-\frac{V(x)}{k_B T}}\; dx = 1$$

Expanding $V(x)$ around the left bottom x_a

$$V(x) = V(x_a) + \frac{1}{2}V''(x_a)(x - x_a)^2$$

we have [write $V''(x_a) = \omega_a^2$]

$$Z\,\sqrt{2\pi k_B T}\, e^{-\frac{V(x_a)}{k_B T}}\;\int_{-\infty}^{b} e^{-\frac{\omega_a^2(x-x_a)^2}{2k_B T}}\; dx = 1$$

$$\text{or} \;\; Z\,\sqrt{2\pi k_B T}\;\frac{\sqrt{2\pi k_B T}}{\omega_a}\; e^{-\frac{V(x_a)}{k_B T}} = 1$$

$$\text{or} \;\; Z = \frac{\omega_a}{2\pi k_B T}\; e^{\frac{V(x_a)}{k_B T}} \quad , \quad [B \to +\infty]$$

Therefore the escape rate k over the barrier is obtained by computing the outward flow over the top of the barrier.

$$k = \int_0^{\infty} v\; P(x_b, v)\; dv$$

Thus we have

$$P(x_b, v) = Z\; e^{-\frac{\frac{1}{2}v^2+V(x_b)}{k_B T}}$$

and k as

$$k = Z\; e^{-\frac{V(x_b)}{k_B T}}\;\int_0^{\infty} v\; e^{-\frac{v^2}{2k_B T}}\; dv$$
$$= Z\; e^{-\frac{V(x_b)}{k_B T}}\;(k_B T)$$

Putting the value of Z in the above equation we get

$$k = \frac{\omega_a}{2\pi k_B T}\, e^{-\frac{[V(x_b)-V(x_a)]}{k_B T}}\; k_B T$$
$$k = \frac{\omega_a}{2\pi}\, e^{-E_0/k_B T}$$

where $E_0 = V(x_b) - V(x_a)$ is the activation energy.

This is the transition state result we derived earlier employing Kramers' method $\gamma = 0$ (Note that this is not a dynamical theory like that of Kramers. So γ does not appear in the theory. For $\gamma \to 0$, one has to consider the problem of energy diffusion. We state the main result; the rate constant k becomes proportional to γ in this limit). This result implies that whenever the Brownian particle is at the top with positive velocity it will escape as if there is an absorbing wall at the barrier top. A rough interpretation of this transition state result is that the particle oscillates in an effective potential $\frac{1}{2}\omega_a^2(x-x_a)^2$ provided by the left well and therefore hit the wall $\omega_a/2\pi$ times per second and each time has a probability $e^{-E_0/k_B T}$ to cross over it.

V. OVERDAMPED MOTION : SMOLUCHOWSKI EQUATION AND DIFFUSION OVER A BARRIER

A. Smoluchowski equation

We wish to derive an equation of diffusion for an ensemble of particles with probability distribution function $f(x,t)$, where the particles in addition to Brownian motion execute a deterministic motion in a force field. The potential is given by $V(x)$. The evolution of distribution from time t to another time $t+\tau$ is given by the following equation

$$f(x, t+\tau) = \int_{-\infty}^{+\infty} f(x-\Delta, t)\, \phi(\Delta)\, d\Delta \quad . \tag{1}$$

In presence of Brownian motion, and under the influence of potential $V(x)$ the equation of motion for the particle of unit mass ($m = 1$) is given by

$$\ddot{x} + \gamma\dot{x} + V'(x) = F(t) \tag{2}$$

where $F(t)$ is the random force term.

Under overdamped condition $\ddot{x} \ll \gamma\dot{x}$ we write

$$\gamma\dot{x} = -V'(x) + F(t) \tag{3}$$
$$\text{or, }\; \dot{x} = -\frac{V'(x)}{\gamma} + \frac{F(t)}{\gamma} \quad . \tag{4}$$

The deterministic increment in x in time τ corresponding to first term on the R.H.S. of Eq.(4) can be calculated as

$$\frac{\partial x}{\partial t}\,\tau = -\frac{V'(x)}{\gamma}\,\tau \quad . \tag{5}$$

Expanding the functions f on both sides of Eq.(1) as usual we have

$$\begin{aligned} & f(x,t) + \frac{\partial f}{\partial t}\,\tau + \frac{\partial f}{\partial x}\left(\frac{\partial x}{\partial t}\right)\tau \\ &= \int_{-\infty}^{+\infty}\left[\, f(x,t) - \frac{\partial f}{\partial x}\,\Delta + \frac{1}{2}\Delta^2\,\frac{\partial^2 f}{\partial x^2}\,\right]\phi(\Delta)\, d\Delta \\ &= f(x,t)\int_{-\infty}^{+\infty}\phi(\Delta)\, d\Delta - \frac{\partial f}{\partial x}\int_{-\infty}^{+\infty}\Delta\,\phi(\Delta)\, d\Delta + \frac{\partial^2 f}{\partial x^2}\int_{-\infty}^{+\infty}\frac{1}{2}\Delta^2\,\phi(\Delta)\, d\Delta \quad . \end{aligned} \tag{6}$$

We now note

$$\left.\begin{array}{rcl} \int_{-\infty}^{+\infty}\phi(\Delta)\, d\Delta & = & 1 \\ \int_{-\infty}^{+\infty}\Delta\,\phi(\Delta)\, d\Delta & = & 0 \\ \frac{1}{2\tau}\int_{-\infty}^{+\infty}\Delta^2\,\phi(\Delta)\, d\Delta & = & D \end{array}\right\} \quad . \tag{7}$$

Putting Eq.(5) in Eq.(6) and making use of Eq.(7) we get

$$\frac{\partial f}{\partial t} = -\frac{\partial f}{\partial x}\,\left(-\frac{V'(x)}{\gamma}\right) + D\,\frac{\partial^2 f}{\partial x^2}$$

or

$$\frac{\partial f}{\partial t} = \frac{\partial f}{\partial x}\,\left(\frac{V'(x)}{\gamma}\right) + D\,\frac{\partial^2 f}{\partial x^2} \tag{8}$$

where D is the diffusion coefficient (position) and is given by $k_B T/\gamma$ as derived earlier (Einstein's theory). This equation is known as Smoluchowski equation.

B. Diffusion of particles over the barrier

We consider a particle moving in a potential field $V(x)$ of the type shown in the Fig.(..). More generally, we may consider an ensemble of particles moving in the potential field $V(x)$ without any mutual interference. We suppose that the particles are initially caught in the potential hole at x_{min}. The general problem we wish to solve is the rate at which particles will escape over the potential barrier as a consequence of Brownian motion.

The problem is very complex. However, considerable simplification can be made if we assume that the height of the potential barrier is large compared to the energy of the thermal motions, i.e., $E_0 \gg k_B T$. Under this circumstance, the problem can be treated in which the conditions are *quasi-stationary*.

More specifically we may suppose that to a high degree of accuracy an equilibrium distribution exists in the neighborhood of x_{min}. But this distribution is not valid for all values of x. We assume that beyond x_{max} the density of particles is very small compared to the equilibrium value. And in consequence of this there will be slow diffusion of particles across x_{max} tending to restore the equilibrium throughout. If the barrier were sufficiently high this diffusion will take place as though the stationarity prevailed. This condition is termed as a quasi-stationary condition.

We thus consider the Smoluchowski equation,

$$\frac{\partial f(x,t)}{\partial t} = \frac{\partial f}{\partial x}\left(\frac{V'(x)}{\gamma}\right) + \frac{k_B T}{\gamma}\,\frac{\partial^2 f(x,t)}{\partial x^2} \quad . \tag{9}$$

Recasting the above equation in the form of a continuity equation we identify j as the current

$$\begin{aligned}\frac{\partial f}{\partial t} &= -\frac{\partial}{\partial x}\left[-\frac{V'(x)f(x,t)}{\gamma} - \frac{k_B T}{\gamma}\,\frac{\partial f(x,t)}{\partial x}\right] \\ &= -\frac{\partial}{\partial x} j(x,t) \quad .\end{aligned} \tag{10}$$

In the stationary state j =constant, i.e., $\frac{\partial f}{\partial t} = 0$, where

$$-\,j = \frac{V'(x)f(x,t)}{\gamma} + \frac{k_B T}{\gamma}\,\frac{\partial f}{\partial x} \quad . \tag{11}$$

Rearranging the above equation as

$$\frac{\partial f(x)}{\partial x} + \frac{V'(x)f(x)}{k_B T} = -\frac{j\gamma}{k_B T} \quad , \tag{12}$$

and integrating between x_{min} to A with the integrating factor

$$e^{+\int \frac{V'(x)}{k_B T}\,dx}\,\left[= e^{+\frac{V(x)}{k_B T}}\right]$$

the equation (12) in the following form

$$\frac{d}{dx}\left[\,f(x)\,e^{+\frac{V(x)}{k_B T}}\,\right] = -\frac{j\gamma}{k_B T}\,e^{+\frac{V(x)}{k_B T}} \quad , \tag{13}$$

we obtain

$$\left[f(x)\, e^{+\frac{V(x)}{k_BT}} \right]_{x_{min}}^{A} = -\frac{j\gamma}{k_BT} \int_{x_{min}}^{A} e^{+\frac{V(x)}{k_BT}}\, dx \quad . \tag{14}$$

The constant current or flux across x_{max} is

$$j = -\frac{k_BT}{\gamma} \frac{\left[f(x)\, e^{+\frac{V(x)}{k_BT}} \right]_{x_{min}}^{A}}{\int_{x_{min}}^{A} e^{+\frac{V(x)}{k_BT}}\, dx} \quad . \tag{15}$$

Since $f(x)$ at A is zero, i.e., $f(A) = 0$, we have

$$j = \frac{k_BT}{\gamma} \frac{f(x_{min})\, e^{+\frac{V(x_{min})}{k_BT}}}{\int_{x_{min}}^{A} e^{+\frac{V(x)}{k_BT}}\, dx} \quad . \tag{16}$$

Around x_{min}, the current is almost zero. This defines an equilibrium condition in the neighborhood of x_{min}. Thus with $j = 0$ the Smoluchowski equation yields (see Eq.(11))

$$\frac{k_BT}{\gamma} \frac{\partial f}{\partial x} = -\frac{V'(x)}{\gamma}\, f(x) \tag{17}$$

or

$$\frac{\partial f}{\partial x} = -\frac{V'(x)}{k_BT}\, f(x) \quad .$$

Integrating between x_{min} to x (a point in the left well)

$$\ln \frac{f(x)}{f(x_{min})} = -\int_{x_{min}}^{x} \frac{V'(x)}{k_BT}\, dx$$

or

$$\begin{aligned} f(x) &= f(x_{min})\, e^{-\int_{x_{min}}^{x} \frac{V'(x)}{k_BT}\, dx} \\ &= f(x_{min})\, e^{\frac{-V(x)+V(x_{min})}{k_BT}} \end{aligned} \tag{18}$$

The equilibrium population in the left well is given by

$$n_a = \int_{x_1}^{x_2} f(x)\, dx = f(x_{min}) \int_{x_1}^{x_2} e^{\frac{-V(x)+V(x_{min})}{k_BT}}\, dx \tag{19}$$

where x_1 and x_2 are two points around x_{min}.

The rate of escape k is thus given by

$$k = j/n_a \quad . \tag{20}$$

Thus from (16) and (19) we obtain

$$\begin{aligned} k &= \left(\frac{k_BT}{\gamma}\right) \frac{f(x_{min})\, e^{+\frac{V(x_{min})}{k_BT}}}{\int_{x_{min}}^{A} e^{+\frac{V(x)}{k_BT}}\, dx} \frac{1}{f(x_{min}) \int_{x_1}^{x_2} e^{\frac{-V(x)+V(x_{min})}{k_BT}}\, dx} \\ &= \left(\frac{k_BT}{\gamma}\right) \frac{e^{+\frac{V(x_{min})}{k_BT}}}{e^{+\frac{V(x_{min})}{k_BT}}} \frac{1}{\int_{x_{min}}^{A} e^{+\frac{V(x)}{k_BT}}\, dx \int_{x_1}^{x_2} e^{-\frac{V(x)}{k_BT}}\, dx} \quad . \end{aligned}$$

Therefore

$$k = \left(\frac{k_B T}{\gamma}\right) \frac{1}{\int_{x_{min}}^{A} e^{+\frac{V(x)}{k_B T}}\ dx\ \int_{x_1}^{x_2} e^{-\frac{V(x)}{k_B T}}\ dx} \quad . \tag{21}$$

We now make use of the following linearization of $V(x)$ around x_{min} and x_{max}. For the integral

$$\int_{x_{min}}^{A} e^{+\frac{V(x)}{k_B T}}\ dx$$

we use

$$V(x) = E_0 - \frac{1}{2}\ \omega_b^2\ (x - x_{max})^2 \tag{22}$$

and let $x_{min} \longrightarrow -\infty$ and $A \longrightarrow +\infty$. Thus

$$\begin{aligned}\int_{-\infty}^{+\infty} e^{+\frac{[E_0 - \frac{1}{2}\omega_b^2 (x-x_{max})^2]}{k_B T}}\ dx &= e^{+\frac{E_0}{k_B T}} \int_{-\infty}^{+\infty} e^{-\frac{(x-x_{max})^2}{2k_B T/\omega_b^2}}\ dx \\ &= e^{+\frac{E_0}{k_B T}}\ \frac{\sqrt{2k_B T}\ \sqrt{\pi}}{\omega_b} \quad .\end{aligned} \tag{23}$$

For the integral

$$\int_{x_1}^{x_2} e^{-\frac{V(x)}{k_B T}}\ dx$$

we use

$$V(x) = \frac{1}{2}\ \omega_0^2\ (x - x_{min})^2 \tag{24}$$

and let

$$\begin{aligned} x_1 &\longrightarrow -\infty \\ x_2 &\longrightarrow +\infty \end{aligned}$$

Therefore

$$\int_{-\infty}^{+\infty} e^{-\frac{1}{2}\frac{\omega_0^2}{k_B T}(x-x_{min})^2}\ dx = \frac{\sqrt{2k_B T}\ \sqrt{\pi}}{\omega_0} \quad . \tag{25}$$

Putting the values of these integrals (23) and (25) in the expression for k in Eq.(21) we obtain

$$\begin{aligned} k &= \frac{k_B T}{\gamma}\ \frac{e^{-\frac{E_0}{k_B T}}}{\left(\frac{\sqrt{2k_B T}}{\omega_b}\right)\ \left(\frac{\sqrt{2k_B T}}{\omega_0}\right)\ \pi} \\ &= \frac{\omega_0\ \omega_b}{2\ \pi\ \gamma}\ e^{-E_0/k_B T} \quad . \end{aligned} \tag{26}$$

i) The rate of activation has a typical Arhenius form $Ae^{-E_0/k_B T}$.
ii) The rate is thus inversely proportional to the friction coefficient of the medium.

VI. THE MASTER EQUATION

A. Master equation

In statistical mechanics we deal with probability distribution functions. The master equation is a typical probability balance equation.

Let us recall the good old theory of Brownian motion. Suppose a series of observations of the same Brownian particle gives a sequence of positions x_1, x_2, x_3, $\ldots$.

Each displacement $x_{k+1} - x_k$ is an element of chance, i.e., is independent of earlier positions x_{k-1}, x_{k-2}, etc. This means probability distribution function does not depend on the previous history. Thus the position x_{k+1} depends only on x_k. We call this stochastic process a *Markov Process*. Since many collision have already occurred during the displacement $x_{k+1} - x_k$, this displacement is much larger than the mean free path.

We now recall the basic equation for evolution of probability (Einstein) distribution function $f(x,t)$.

$$f(x, t+\tau) = \int f(x+\Delta, t)\ \phi(\Delta)\ d\Delta \tag{1}$$

This equation relates the probability distribution function of a Brownian particle at x and time $t+\tau$, to that for the particle at a previous position $x+\Delta$ at an earlier time t. $\phi(\Delta)$ is the probability of a jump of magnitude Δ (i.e., $x_{k+1} - x_k$) in the picture from $x+\Delta$ to x.

We now introduce the following notation for convenience. We denote

$$y = x + \Delta \tag{2}$$

and therefore, $dy = d\Delta$.
Also write

$$\phi(\Delta) = \phi(x \to y)\ \ , \tag{3}$$

where the arrow refers to the direction of jump from $x \to y$. Eqn.(1) can then be rewritten as [denote $f(x,t)$ by $P(x,t)$]

$$P(x, t+\tau) = \int \phi(y \to x)\ P(y,t)\ dy\ \ . \tag{4}$$

Expanding the left hand side as before we write

$$P(x,t) + \tau \frac{\partial P(x,t)}{\partial t} = \int \phi(y \to x)\ P(y,t)\ dy\ \ . \tag{5}$$

Rearranging

$$\tau \frac{\partial P(x,t)}{\partial t} = \int \phi(y \to x)\ P(y,t)\ dy - P(x,t)\ \ . \tag{6}$$

Now note that

$$\begin{aligned} \int \phi(x \to y)\ dy &= \int \phi(-\Delta)\ d\Delta \\ &= 1 \end{aligned} \tag{7}$$

(Normalization of probability).

Therefore we write

$$P(x,t) = \int \phi(x \to y)\ P(x,t)\ dy \tag{8}$$

Putting (8) in (6) we get

$$\tau \frac{\partial P(x,t)}{\partial t} = \int \phi(y \to x)\ P(y,t)\ dy - \int \phi(x \to y)\ P(x,t)\ dy \tag{9}$$

Dividing both sides by τ and rewriting

$$W(y \to x) = \frac{\phi(y \to x)}{\tau} \tag{10}$$

we get

$$\frac{dP(x,t)}{dt} = \int W(y \to x)\ P(y,t)\ dy - \int W(x \to y)\ P(x,t)\ dy \tag{11}$$

$W(y \to x)$ is the probability of a jump from $y \to x$ per unit time or the transition probability per unit time.

The above equation is called the master equation. One can immediately write a discrete version of this equation as [replace y by n, x by m and integral by summation]

$$\frac{dP_m(t)}{dt} = \sum_n W_{nm}\ P_n(t) - \sum_n W_{mn}\ P_m(t) \tag{12}$$

In this form the meaning of master equation in very clear The first term is the gain of state m due to transitions from the other states n and the second term is the loss due to transitions from m to all other states n. Note that $W_{nm} \geq 0$ when $n \neq m$. The master equation is thus a loss-gain equation for probabilities of separate states.

The master equation is a doorway for studying the approach to equilibrium. The condition for equilibrium is defined as $\frac{dp_m}{dt} = 0$, i.e.,

$$\sum_n W_{nm}\ P_n^{eq} = \sum_n W_{mn}\ P_m^{eq}$$

$P_i^{eq}(i = m \text{ or } n)$ must be identified with the equilibrium distribution function known from equilibrium statistical mechanics.

The above condition states the fact that *in equilibrium* the sum of all transitions per unit time into any state m must be balanced by the sum of all transitions from m to all other states n. We now state another stronger condition that for each pair n, m separately the transitions must balance.

$$W_{nm}\ P_n^{eq} = W_{mn}\ P_m^{eq}$$

This is the principle of detailed balance and is true for all closed, isolated systems.

B. Applications

One step process : If we consider the jumps only between the nearest neighboring sites then the process is called an one-step process.

The coefficient r_n is the probability/time that being at n, a jump to $n-1$ has occurred and g_n is probability/time for a jump to $n+1$ from n. For this the master equation (12) reduces to

$$\dot{p}_n = g_{n-1}\ p_{n-1} + r_{n+1}\ p_{n+1} - (r_n p_n + g_n p_n) \tag{13}$$

1. Example 1 : unidirectional random walk

Consider a one step process with constant transition probability.

$$r_n = 0 \ \ , \ \ g_n = q \tag{14}$$

The master equation is

$$\dot{p}_n = q(p_{n-1} - p_n) \tag{15}$$

It is a random walk over integers $n = 0, 1, 2, \ldots$ with steps only to the right at random times. We start with a trial solution

$$p_n = \alpha_n(t)\ e^{-qt} \ \ . \tag{16}$$

where $\alpha_n(t)$ is to be determined.
Hence putting (16) in (15) we obtain

$$\begin{aligned} \dot{\alpha}_n &= q\ \alpha_{n-1} \\ \dot{\alpha}_{n-1} &= q\ \alpha_{n-2} \\ \vdots &= \vdots \\ \dot{\alpha}_2 &= q\ \alpha_1 \\ \dot{\alpha}_1 &= q\ \alpha_0 \end{aligned}$$

Assume $\alpha_0(t=0)=1$ i.e., $p_0(t=0)=1$ as the initial condition imposed on (16). Therefore

$$\begin{aligned}\alpha_1 &= q\ t \\ \dot{\alpha}_2 &= q\ \alpha_1 = q^2\ t\end{aligned}$$

which leads to

$$\begin{aligned}\alpha_2 &= q^2\ t^2/2 \\ \vdots &= \vdots \\ \alpha_n &= q^n\ t^n/n!\end{aligned}$$

Therefore the solution is

$$p_n(t) = \frac{q^n\ t^n}{n!}\ e^{-q\ t} \tag{17}$$

which is a Poisson distribution. Note that it is a non-stationary distribution. In the next example we consider a wellknown stationary distribution.

2. *Example 2 : quantized harmonic oscillator interacting with a radiation field*

Consider $n=0,1,2,\ldots$ states of a harmonic oscillator. The oscillator is interacting with a radiation field. The interaction between the oscillator and the radiation field is causing the transition between the states of the oscillator. Energy of a state n is

$$\left(n+\frac{1}{2}\right)\ h\ \nu \tag{18}$$

Since the dipole moment matrix element between $n-1$ and n is proportional to n, probability for a jump from $n-1 \to n$

$$g_{n-1} = \beta\ n \tag{19}$$

Probability of a jump from $n \to n-1$

$$r_n = \alpha\ n \tag{20}$$

α, β are dependent on the frequency of light. We start from

$$\begin{aligned}&\dot{p}_n = g_{n-1}\ p_{n-1} + r_{n+1}\ p_{n+1} - (g_n + r_n)\ p_n \\ &\dot{p}_n = \beta\ n\ p_{n-1} + \alpha(n+1)\ p_{n+1} - [\beta(n+1) + \alpha\ n]\ p_n\end{aligned} \tag{21}$$

For a stationary distribution $\dot{p}_n = 0$. Therefore we have

$$0 = \beta\ n\ p_{n-1} + \alpha(n+1)\ p_{n+1} - [\beta(n+1) + \alpha\ n]\ p_n$$

$$\beta\ (n+1)\ p_n - \alpha(n+1)\ p_{n+1} = \beta\ n\ p_{n-1} - \alpha\ n\ p_n = \text{const} = 0\ \ . \tag{22}$$

Hence

$$\beta\ p_{n-1} = \alpha\ p_n$$

Therefore

$$p_n = \frac{\beta}{\alpha}\ p_{n-1}$$

which we rewrite as

$$p_n = \left(\frac{\beta}{\alpha}\right)^n p_0 \quad , \quad p_0 = \text{constant} \tag{23}$$

This distribution is an equilibrium distribution. We know from equilibrium statistical mechanics that

$$p_n = \text{const} \times e^{-nh\nu/kT} \tag{24}$$

Therefore equating (23) and (24) we obtain

$$\left(\frac{\beta}{\alpha}\right)^n = \left(e^{-h\nu/kT}\right)^n$$
$$\text{or} \;\; \frac{\beta}{\alpha} = e^{-h\nu/kT}$$

Since g_n is proportional to the radiation density ρ present

$$\beta = C\ \rho$$

For r_n which is given by α there are spontaneous (A) and stimulated processes ($B\rho$),

$$\alpha = B\rho + A$$

Therefore we have

$$\frac{A + B\rho}{C\rho} = e^{-h\nu/kT}$$

Rearranging we write

$$\rho = \frac{A}{Ce^{-h\nu/kT} - B} \tag{25}$$

which has the form of a Planck's distribution. A, B and C can be determined by comparing with Rayleigh-Jeans law and the Wein's law in long wavelength and short wavelength limits.

APPENDIX A: EVALUATION OF EQ.(17)

$$\begin{aligned}
f(x,t) &= \frac{n}{2\pi}\int_{-\infty}^{+\infty} e^{ikx}\ e^{-k^2Dt}\ dk \\
&= \frac{n}{2\pi}\ e^{-x^2/4Dt}\int_{-\infty}^{+\infty} e^{ikx}\ e^{(k\sqrt{Dt})^2}\ e^{x^2/4Dt}\ dk \\
&= \frac{n}{2\pi}\ e^{-x^2/4Dt}\int_{-\infty}^{+\infty} \exp\left[-\left\{(k\sqrt{Dt})^2 + (-ix/2\sqrt{Dt})^2 + (-ikx)\right\}\right]\ dk \\
&= \frac{n}{2\pi}\ e^{-x^2/4Dt}\int_{-\infty}^{+\infty} \exp\left[-(k\sqrt{Dt} - (ix/2\sqrt{Dt}))^2\right]\ dk \\
&= \frac{n}{2\pi}\ e^{-x^2/4Dt}\int_{-\infty}^{+\infty} \frac{1}{\sqrt{Dt}}\ e^{-y^2}\ dy\ \ ;\ \ \text{put } y = k\sqrt{Dt} - (ix/2\sqrt{Dt}),\ dy = \sqrt{Dt}\ dk \\
&= \frac{n}{2\pi\sqrt{Dt}}\ e^{-x^2/4Dt}\ \sqrt{\pi} \\
f(x,t) &= \frac{n}{\sqrt{4\pi Dt}}\ e^{-x^2/4Dt} \quad .
\end{aligned}$$

This result shows that a Fourier transform of a Gaussian function is a Gaussian.

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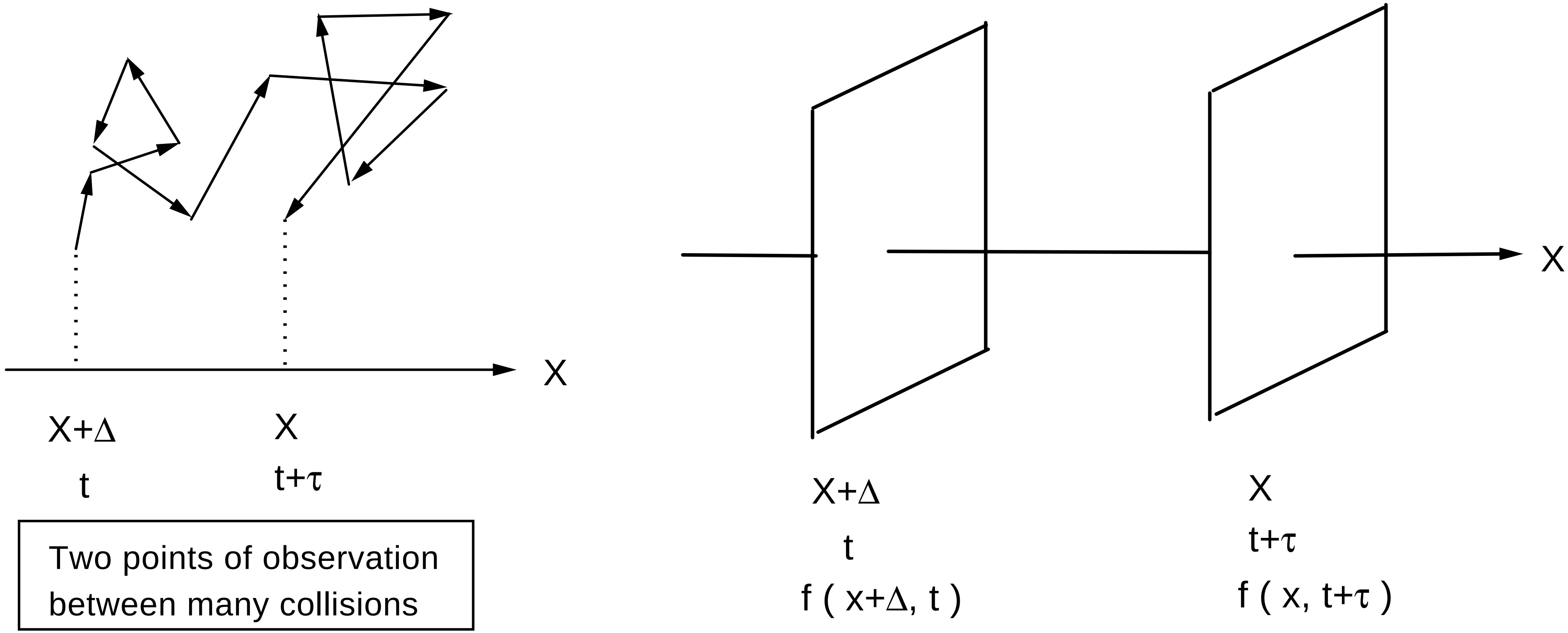
X
X+Δ
t
X
t+τ
Two points of observation
between many collisions
X
X+Δ
t
f (x+Δ, t)
X
t+τ
f (x, t+τ)

Fig.(1)

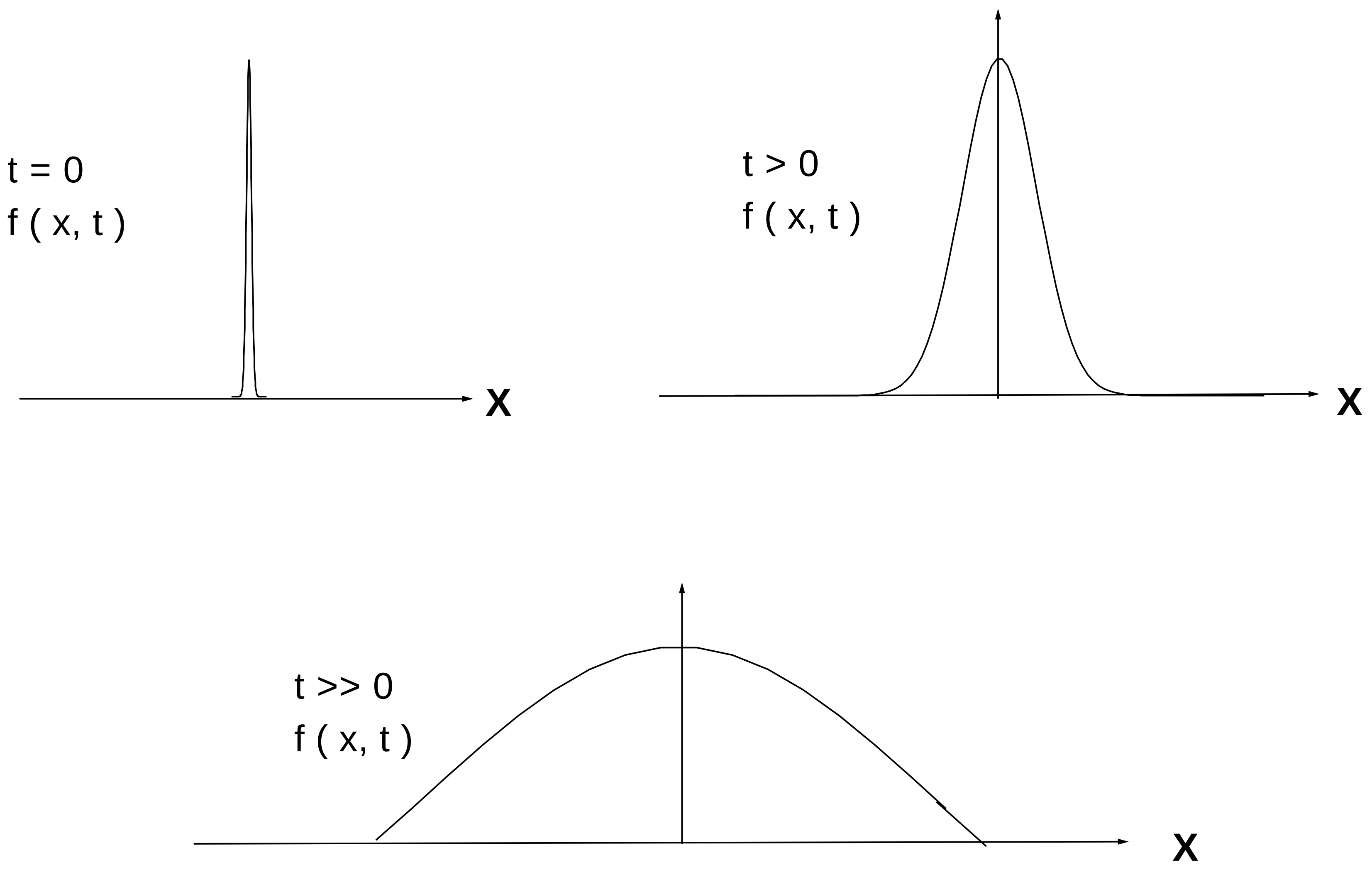

Fig.(2)

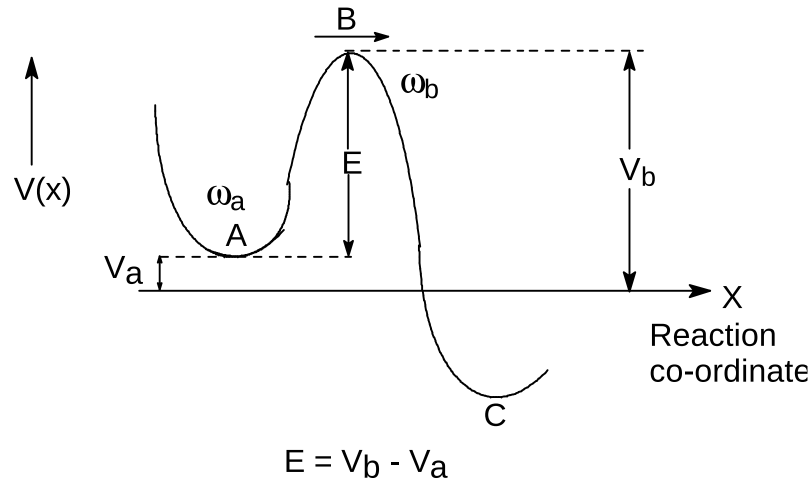

Fig.(3)

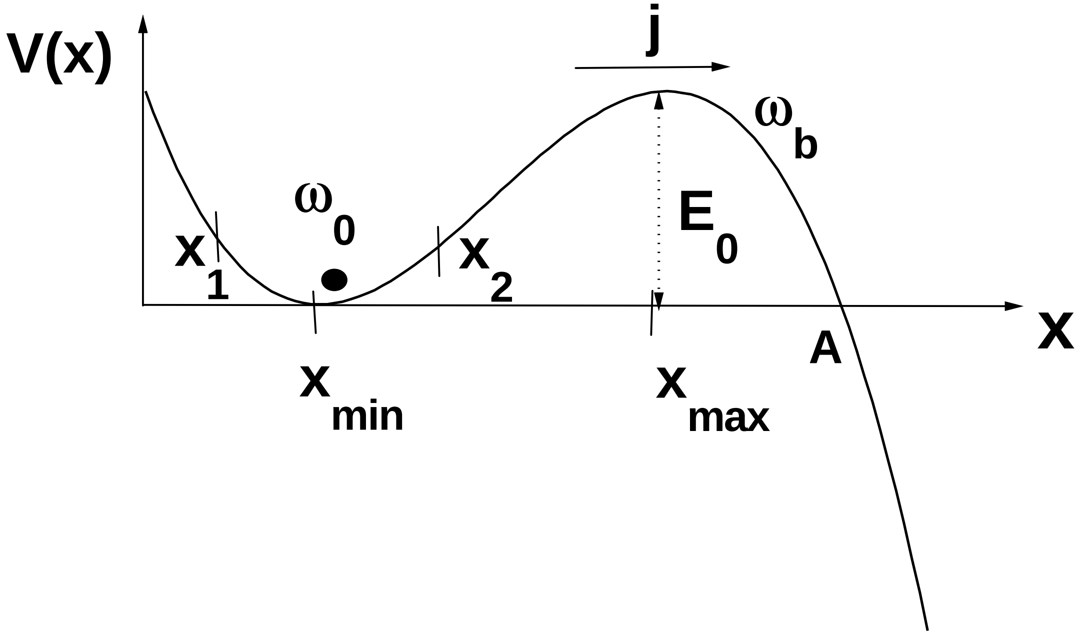

Fig.(4)

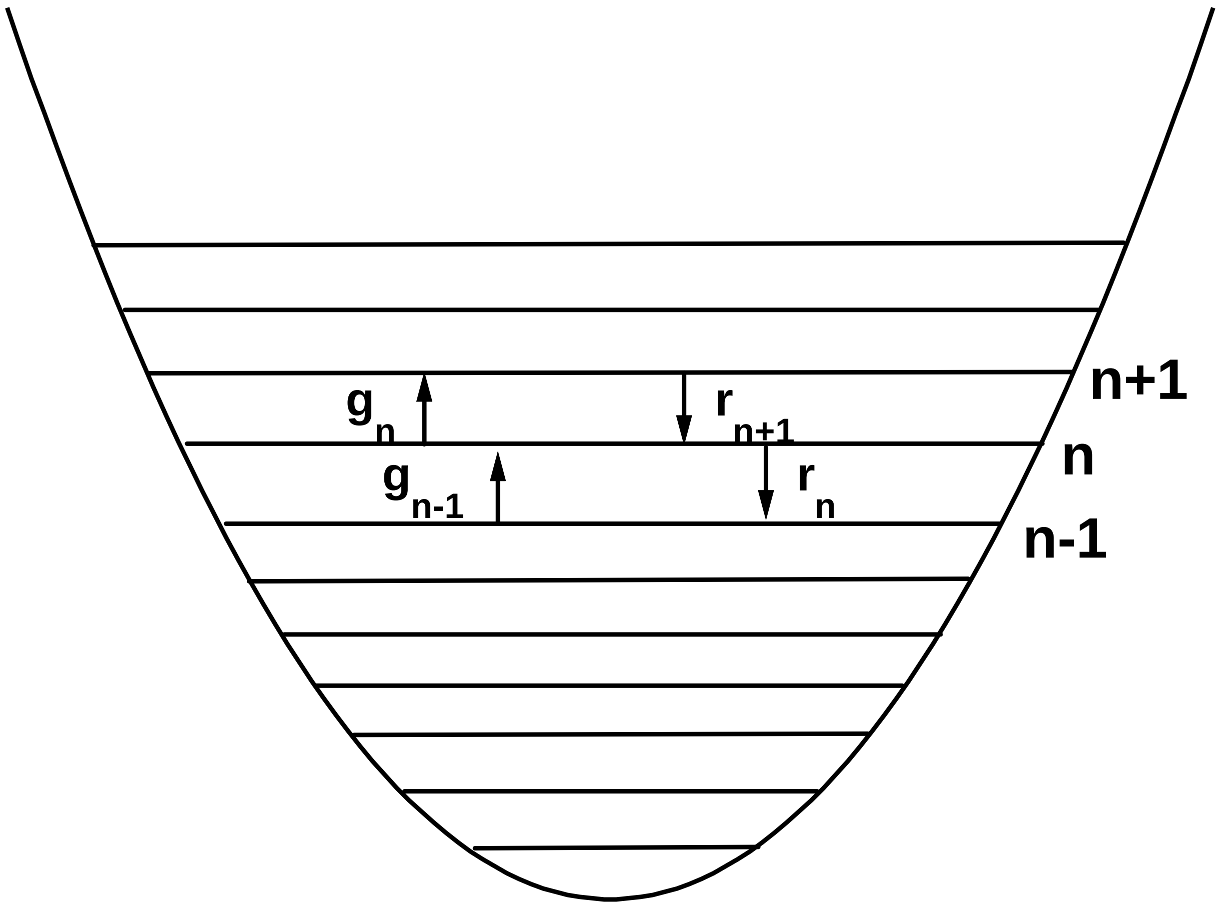

Fig.(8)

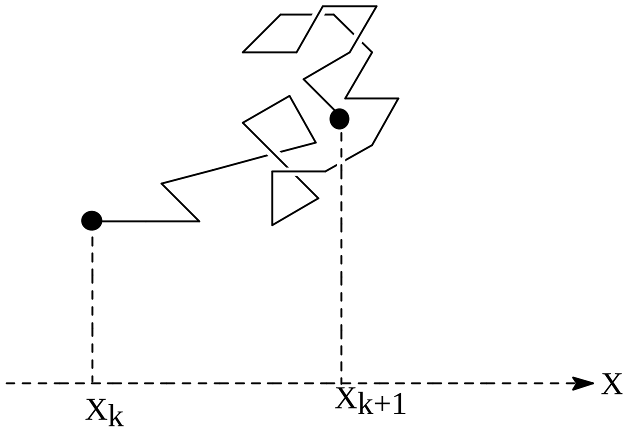

Fig.(5)

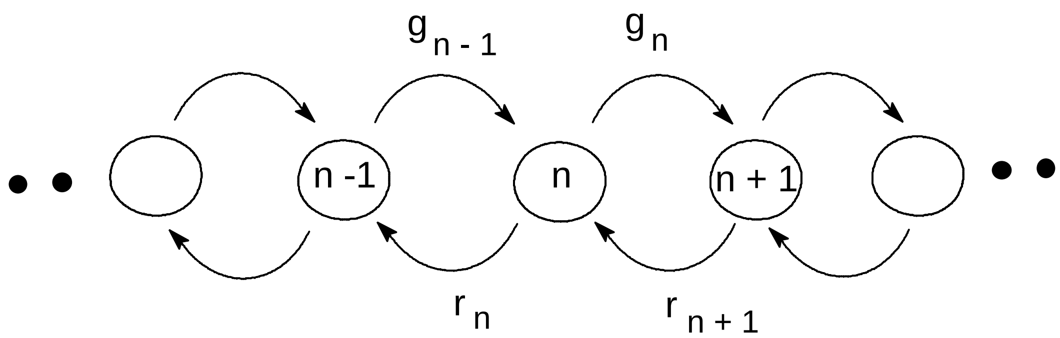

Fig.(6)